Engineering of efficient phosphorescent iridium cationic complex for developing oxygen-sensitive polymeric and nanostructured films

Antonio L. Medina-Castillo^a, Jorge F. Fernández-Sánchez^{*,a,b} Cédric Klein^c, Mohammad K. Nazeeruddin^c, Antonio Segura-Carretero^a, Alberto Fernández-Gutiérrez^{*,a}, Michael Graetzel^c, Ursula E. Spichiger-Keller^b

^aDepartment of Analytical Chemistry, Faculty of Sciences, University of Granada. C/Fuentenueva s/n E-18071, Granada, Spain. Centre for Chemical Sensors, Swiss ^bFederal Institute of Technology Zurich (ETH-Z), Technoparkstrasse 1, CH-8005, Zurich, Switzerland. Laboratory for Photonics and Interfaces. Institute of Chemical ^cSciences and Engineering. Ecole Polytechnique Fédérale de Lausanne (EPFL). CH-1015 Lausanne, Switzerland.

*J.F. Fernandez-Sanchez: E-mail: jffernan@ugr.es. Fax: +34 958249510. Phone: +34 958248593; A. Fernandez-Gutierrez: E-mail: <u>albertof@ugr.es</u>. Fax: +34 958249510. Phone: +34 958243297.

In this study, a novel phosphorescent Ir(III)complex [Ir(2-phenylpyridine)2(4,4'-bis(2-(4-N,N-methylhexylaminophenyl)ethyl)-2-2'-bypyridine)Cl] (for convenience, the complex was given the synonym N-948) has been designed and synthesized, to be used as an oxygen-probe. It was characterized by spectroscopic and analytical methods when incorporated in polystyrene and nanostructured metal oxide support. N-948 is the first Ir complex in the literature with a luminescence emission at a wavelength higher than 650 nm, (665 nm), with a quantum yield higher than 0.50 (0.58 \pm 0.05) and an extremely long phosphorescence lifetime (102 μ s) which has been used for developing oxygensensitive films. In addition, the new complex shows a Stern-Volmer constant which is 20 times higher than that of other Ir complexes known from the literature. The complex shows long-term stability (up to 12 months), complete reversibility of the signal quenched by oxygen and quick response time to various oxygen concentrations (<0.5s). Thus, it is an interesting and promising complex for developing oxygen-selective sensors for gas analysis and the analysis of dissolved oxygen.

1. Introduction

Molecular oxygen is one of the most important gases in our environment since it is involved as either a reactant or a product in a vast number of chemical and biochemical processes.¹⁻¹¹

Several oxygen detection systems have been reported but most of them show some limitations since they consume oxygen, show a relatively long response time and are chemically unstable which make these systems not suitable as disposable sensors.¹⁰ The development of *in-situ* and real-time field measurement systems using (bio)chemical sensors are an elegant alternative to the in-lab monitoring system currently employed. Therefore, a variety of optical devices and sensors have been developed to measure molecular oxygen. These optical devices are based on quenching of the luminescence of organometallic complexes (OMCs) by paramagnetic oxygen.^{12,13} Bimolecular collisions between the excited OMCs and the ground state (triplet) oxygen relax the luminophore nonradiatively and produce singlet oxygen.¹⁴ Fernandez-Sanchez *et al.*¹⁰ summarized in an overview the most representative OMCs used for developing optical oxygen-sensing layers.

Preferably, an OMC which may be used for the measurement of the partial pressure of oxygen, pO_2 , by luminescence quenching must show a high luminescence quantum yield; the use of compounds which show typically a high luminescence quantum yield as potential oxygen sensors are less affected by interferences, thus permitting the use of less sensitive detectors in the development of optical oxygen sensors. In addition, they must show a high photo-stability, long lifetime of the excited state, strong absorption bands in the visible range of the electromagnetic spectrum, large Stokes' shift, fast response time and a high Stern-Volmer constant (sensitivity to O_2).¹¹ In addition, for biological applications, they must emit at an emission wavelength longer than 650 nm to be more compatible with current solid-state optoelectronics¹⁵ and to avoid interference of biological molecules which usually emit between 550 and 600 nm.

Although Ir complexes have shown very promising characteristics to be used as oxygen probes^{10,16-31} they are the least-studied OMCs compared with Ru, Pd or Pt-OMCs among others. Iridium complexes show high luminescence quantum yields, are photo-stable and have long decay times (luminescence lifetimes), strong absorption bands, large Stokes' shift, fast response time and a high Stern-Volmer constant.^{10,11} But,

the main inconvenience of these Ir-complexes for the development of oxygen-sensitive films is their emission wavelengths, which are shorter than 650 nm. Anyway, several novel Ir(III) complexes which have emission wavelength larger than 650 haven been proposed recently. Electronic supporting information (ESI) shows a table with the luminescent properties of the most representatives Ir-complexes which have been used or could be used as oxygen probes.

It shows that Ir complexes usually emit at a wavelength shorter than 650 nm or, if the wavelength is longer than 650 nm, the luminescence quantum yields are low. Thus, few luminophores can emit phosphorescence with both an emission wavelength higher than 650 nm and a quantum yield higher than 50% and none of them have been tested as oxygen-sensitive dyes so far.

In this paper, we propose a highly phosphorescent iridium complex, namely N-948 [Ir(2-phenylpyridine)₂(4,4'-bis(2-(4-N,N-methylhexylaminophenyl)ethyl)-2-2'bypyridine)Cl], which shows the required characteristics as an oxygen probe incorporated into polystyrene (PS) and/or a nanostructured metal oxide support. These features are: (1) a high luminescence quantum yield: 0.58, (2) long-term stability: up to 12 months, (3) long decay time (luminescence lifetime): 102 μ s, (4) strong absorption bands, (5) large Stokes' shift: 200 nm, (6) fast response time: >0.5s, (7) high Stern-Volmer constant: 60 bar⁻¹ and (8) an emission wavelength of 665 nm. In addition, it has a high lipophilicity which generally improves the retention of the dye in very apolar polymer films, such as those used for chemical sensing.

The N-948 is incorporated into PS, plasticized with and without the plasticizer *o*-cyanophenyl octyl ether (*o*-CPOE) as a solvent, and in a nanostructured solid-support which was proposed for developing gas-sensitive films.^{11,32-34} PS was used to provide mechanical strength to the film and to permit the sterilization by heat. The Stern-Volmer constants of the different films were investigated by intensity and decay time (luminescence lifetime) measurements and the results of different types of optodes are compared.

2. Methodology

2.1. Materials.

All the chemicals and the solvents were received from Fluka and used as received. For the preparations of the nanostructured solid-support, AlOOH Dispersal 100/2 (Sasol GmbH, Germany), acetic acid (Ardrich), polyvinyl alcohol (PVA; 85,000-146,000 molecular weight, Aldrich) and transparent polyester (PET) support 175µm thick (P72, Dupont) were used.

For the preparations and characterization of the membranes, synthesized dye was used as well as chloroform (HPLC grade, Fluka), Rhodamine 101 (Fluka), polystyrene (PS; Scientific Polymers, USA) and *o*-cyanophenyl octyl ether (*o*-CPOE; Fluka, puriss).

The gas flow-system was supplied by 50L gas bottles at 200 bars with nitrogen 60 and oxygen 55 (both from Carbagas).

2.2. N,N-methylhexylaniline.

N-methylaniline (5 g, 46.7 mmol), 1-bromohexane (7.76 g, 47 mmol) and K₂CO₃ (7 g, 50.6 mmol) were refluxed overnight in acetonitrile (100 ml) under nitrogen. After being cooled to room temperature, acetonitrile was evaporated, water (100 ml) was added and extracted with Et₂O (2×100 ml). The combined organic fractions were washed with water (2×100 ml), dried over MgSO₄, filtered and evaporated to dryness. The crude product was purified by column chromatography (SiO₂, hexane/CH₂Cl₂, 9/1) to afford 4.6 g (52%) of *N*,*N*-methylhexylaniline as a slightly yellow oil. ¹H-NMR (CDCl₃, 298K, 200 MHz, δ ppm) 0.92 (t, *J* = 6.4 Hz, 3H), 1.2-1.3 (m, 6H), 1.57 (m, 2H), 2.95 (s, 3H), 3.32 (t, *J* = 6.5 Hz, 2H), 6.72 (m, 3H), 7.25 (m, 2H). ¹³C-NMR (CDCl₃, 298K, 50 MHz, δ ppm) 14.0, 22.7, 26.6, 26.9, 31.7, 38.2, 52.8, 112.1, 115.8, 129.1, 149.4.

2.3. N,N-methylhexylaminobenzaldehyde.

POCl₃ (4.42 g, 28.8 mmol) was dropwise added to a solution *N*,*N*-methylhexylaniline (4.6 g, 24 mmol) in anh. DMF (5 ml) at 0°C under nitrogen. The resulting solution was stirred at 70°C for 3 hours. After being cooled to room temperature, Et₂O (100 ml) and

aqueous NaOAc solution (8 g in 50 ml) were added and stirring was continued overnight at room temperature. The organic layer was separated and the aqueous layer extracted with Et₂O (100 ml). The combined organic fractions were washed with water (2×100 ml) and brine (50 ml), dried over MgSO₄, filtered and evaporated to dryness. The crude product was purified by column chromatography (SiO₂, CH₂Cl₂) to afford 4 g (76%) of *N*,*N*-methylhexylaminobenzaldehyde as a slightly yellow oil. ¹H-NMR (CDCl₃, 298K, 200 MHz, δ ppm) 0.87 (t, *J* = 6.4 Hz, 3H), 1.2-1.3 (m, 6H), 1.57 (m, 2H), 3.00 (s, 3H), 3.35 (t, *J* = 6.5 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 9.68 (s, 1H). ¹³C-NMR (CDCl₃, 298K, 50 MHz, δ ppm) 14.0, 22.6, 26.6, 26.8, 31.6, 38.4, 52.4, 110.7, 124.8, 132.0, 153.4, 189.9.

2.4. 4,4'-bis(2-(4-N,N-methylhexylaminophenyl)ethenyl)-2,2'-bipyridine.

To a solution of 4,4'-bis(diethylmethylphosphonate)-2,2'-bipyridine¹⁷ (1 g, 2.2 mmol) and *N*,*N*-methylhexylaminobenzaldehyde (2.5 eq.) in anhydrous DMF (50 ml) was added solid *t*-BuOK (4 eq.). The resulting mixture was stirred overnight at room temperature under nitrogen. DMF was evaporated and MeOH (150 ml) was added. The formed precipitate was filtered, washed with small portions of MeOH (3×10 ml) and air-dried to afford pure 4,4'-bis(2-(4-*N*,*N*-methylhexylaminophenyl)ethenyl)-2,2'-bipyridine as a yellow solid in 87% yield. (CDCl₃, 298K, 200 MHz, δ ppm) 0.92 (t, *J* = 6.3 Hz, 6H), 1.2-1.4 (m, 12H), 1.62 (m, 4H), 3.00 (s, 6H), 3.37 (t, *J* = 7 Hz, 4H), 6.69 (d, *J* = 8 Hz, 4H), 6.92 (d, *J* = 16 Hz, 2H), 7.32 (d, *J* = 16 Hz, 2H), 7.36 (d, *J* = 5 Hz, 2H), 7.46 (d, *J* = 8 Hz, 4H), 8.49 (s, 2H), 8.63 (d, *J* = 5 Hz, 2H). ¹³C-NMR (CDCl₃, 298K, 50 MHz, δ ppm) 14.0, 22.6, 26.7, 26.8, 31.7, 38.3, 52.6, 111.8, 117.8, 120.4, 121.0, 123.8, 128.4, 133.5, 146.7, 149.3, 149.6, 156.5. Anal. Calcd for C₄₀H₅₀N4•0.25H₂O: C, 81.24; H, 8.61; N, 9.47. Found: C, 80.96; H, 8.78; N, 9.55.

2.5. [Ir(2-phenylpyridine)₂(4,4'-bis(2-(4-*N*,*N*-methylhexylaminophenyl)ethenyl)-2,2'-bipyridine)] Cl (N-948).

The mixed ligand complex was synthesized in a low boiling solvent dichloromethane by reacting the dichloro-bridged iridium (III) dimer with 4,4'-bis(2-(4-N,N-methylhexylaminophenyl)ethenyl)-2,2'-bipyridine). In a typical synthesis the dimeric

iridium (III) complex [Ir(2-phenyl)pyridine) $_2$ (Cl)] $_2$ (300 mg; 0.28 mM) was dissolved in 100 ml of dichloromethane solvent under nitrogen. To this solution was added 4,4'bis(2-(4-N,N-methylhexylaminophenyl)ethenyl)-2,2'-bipyridine (425 mg, 0.724 mM). The reaction mixture was refluxed under nitrogen for three 3 hours. The solvent dichloromethane was 20 evaporated and the resulting solid was dissolved in 5 mL of methanol and precipitated by ether. Yield: 394 mg; 63%. Anal. Calcd for C₆₂H₆₆ClIrN₆: C, 66.32; H, 5.92; N, 7.48; Found: C, 65.69; H, 6.01; N, 7.84.

2.6. X-ray structural determination.

Diffraction data were collected with $Mo_{K\Box}$ radiation on an Oxford Diffraction diffractometer with kappa geometry, equipped with a Sapphire CCD detector. Data reduction and cell refinement were performed with CrysAlis RED 1.6.9³⁵. Structure was solved with *ab initio* direct methods³⁶ and refined by full-matrix least-squares methods on F2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the riding model with Uiso = aUeq(C) (where a is 1.5 for methyl hydrogen atoms and 1.2 for others and C is the parent carbon atom). Space group determination, structure refinement and geometrical calculation were performed with the SHELXTL software package, release 5.1.³⁷

2.7. Preparation of the nanostructured AP200/19 AlOOH-matrix solid support.

The preparation of the nanostructured matrix was carried out following the procedure proposed by Brugger *et al.*.³⁸ 50 g of the aluminum oxide/hydroxide (AlOOH) DISPERSAL 100/2 (from Sasol GmbH, Hamburg, Germany) was mixed for 15 minutes by vigorous mechanical stirring into 948 g of doubly distilled water at a temperature of 20°C. The temperature was then increased to 90°C and stirring was continued for 15 min at this temperature to enable extensive dispersion in the form of AlOOH nanocrystals. The solid was filtered, washed three times with doubly distilled water and dried at 110°C. 8 g of this solid were added to a mixture of 63 g of doubly distilled water and 0.96 g of concentrated acetic acid 80% (from Aldrich Chemie, Buchs, Switzerland). The resulting dispersion was exposed to ultrasound for 3 min at 40°C. Subsequently 8 g of a solution of polyvinyl alcohol (PVA), 10% by weight and with a molecular weight of 85000 to 146000 (from Aldrich Chemie, Buchs, Switzerland), was

added and the resulting coating solution was again exposed to ultrasound for 3 minutes. Curtain coating was then used to coat a transparent polyester (PET) support 175 μ m thick (from Dupont de Nemours) called P72 with 28.5 g m⁻² of this solution at a temperature of 40 °C. The coated support was then dried for 60 minutes at a temperature of 30°C. The resulted nanostructured solid-support is called AP200/19 and it has the following characteristics: pore volume 0.7 mL g⁻¹, total pore volume 20.0 mL m⁻², pore diameter 19.2 nm

Curtain coating is a technique used in coating photographic materials where a freefalling coating solution (having a curtain-like behavior) is coated without direct contact on the substrate, generally a polyester foil (roll-to-roll coating).

2.8. Membrane preparation and characterization.

The cocktails were prepared in sealable 4 mL flasks and then were filled up to 2 mL solution volume with chloroform. Table 1 shows the composition and the nomenclature of the different cocktails, which were shaken on an IKA-Vibramax-VXR (IKA-Labortechnik, Staufen, Germany) until all components were dissolved. The membranes were obtained using a spin-coating technique. For polystyrene membranes, 0.3 mL of the cocktail was injected onto a rotating glass plate of a spinning device at 350 rpm. The resulting layers showed a thickness between 2-7 μ m, depending on the rotational speed and viscosity of the polymer mixture. For the metal oxide, nanostructured membranes, 0.1 mL of the cocktail was injected onto the rotating metal oxide support fixed onto a spinning device at 150 rpm. Both, PS and AlOOH membranes were transparent and allowed visible light to pass through.

A standard protocol was used for characterizing the membranes. The standard settings for all the experiments were: excitation and emission slits 10 nm wide, excitation wavelengths of 494 nm, emission wavelengths of 665 nm, decay time (t_d) 120µs, gate time (t_g) 5 ms, detector voltage 700V and a flow-rate of 200 mL min⁻¹. To obtain the Stern-Volmer Plot (SVP), the oxygen partial pressures were calculated from the measured oxygen/nitrogen flows, assuming a constant environmental pressure of 1000 mbar. Intensity and lifetime measurements were made at 14 different oxygen partial pressures between 0 and 1 bar.

All the measurements were carried out in triplicate to evaluate the error. The experimental results were expressed as the average of 3 replicas \pm error (), where *s* is the standard deviation, *t* the student t and *n* the number of replicas.

2.9. Instrumentation.

The phosphoresce intensity and lifetime measurements were carried out on a Varian Cary-Eclipse luminescence spectrometer equipped with a Xe flash lamp (peak power equivalent to 75 kW), Czerny-Turner monochromators, R-928 photomultiplier tube which is red sensitive (even 900 nm) with manual or automatic voltage.

A PC-controlled system was designed to control the gas composition. Copper and stainless steel tubing were used to connect the flow-through cell. For gas mixing, two mass flow controllers of Type 1179 from MKS Instruments (Andover, MA, USA) were used. After the mass flow controller, stainless steel tubing was used between the mixing T-union and the two-fold solenoid valve of the Cole-Parmer Instrument (Vernon Hills, IL, USA). The system was controlled by a self-written LabVIEW 5.1 program connected to a National Instrument card with an RS-232 interface, which fully controls the spectrometers via the serial interface and the MKS mass flow controllers via RS-485.

The membrane thickness was measured with a TENCOR alpha-step 200 profilometer (San Jose, CA, USA).

3. Result and discussion

3.1. Synthesis of N-948.

The mixed ligand complex, $[Ir(2-phenylpyridine)_2(4,4'-bis(2-(4-$ *N*,*N*-methylhexylaminophenyl)ethenyl)-2,2'-bipyridine)] Cl (N-948) was synthesized in dichloromethane starting from the dichloro-bridged iridium (III) dimer [Ir₂(2-phenylpyridine)₄(Cl₂)] and 4,4'-bis(2-(4-*N*,*N*-methylhexylaminophenyl)ethenyl)-2,2'-bipyridine)4,4'-dimethylamino-2,2'-bipyridine yielding a red powder. The N-948 complex was recrystallized from methanol ether mixture and characterized by analytical and spectroscopic techniques. The crystal structure of N-948 complex clearly shows that

the pyridine ligands of 2-phenylpyridine are mutually found in trans position and the phenyl carbons are cis-configuration which are trans to the 4,4'-bis(2-(4-*N*,*N*-methylhexylaminophenyl)ethenyl)-2,2'-bipyridine)4,4'-dimethylamino-2,2'-bipyridine ligand (see Fig. 1).

Fig. 2 shows absorption and emission spectra of the cationic N-948 complex measured in dichloromethane solution at 298K. The absorption spectrum displays bands in the UV at 262 (19000 M⁻¹ cm⁻¹), 284 (15000 M⁻¹ cm⁻¹) and 318 (10000 M⁻¹ cm⁻¹) and in the visible region at 394 (11700 M^{-1} cm⁻¹) and 468 (20500 M^{-1} cm⁻¹) nm due to intra ligand $(\pi - \pi^*)$ and metal to ligand charge transfer transitions (MLCT), respectively. The N-948 complex when excited within the MLCT absorption bands at 298 K, shows emission maxima at 690 nm. This effect must be due to the extended aromatic system of the ligand where the bipyridyl group is electronically coupled to the N-phenyl group by the ethenyl bridge: Donor-acceptor system of the ligand in addition to the MLCT. This is a clear red shift of around 140 nm compared to the analogous [Ir(2phenylpyridine)₂(4,4'-*dimethylamino*-2,2'-bipyridine)]Cl and [Ir(2phenylpyridine)₂(2,2'-bipyridine)]Cl complexes. It is worth to note that the argondeaerated dichloromethane solution of N-948 shows bright red luminescence under a UV lamp in a lighted room.

3.2. Spectroscopic behavior of the oxygen-sensitive material.

The dichloromethane solution of N-948 exhibits an intense bright red luminescence maximum at 681 nm upon excitation at the metal-to-ligand charge transfer maxima at 495 nm. It shows a luminescence quantum yield of 0.1 in dichloromethane which is extremely high compared to other Ir-complexes which emit at similar wavelengths. However, the phosphorescence lifetime of the dye in solution has to be lower than 12μ s because it cannot be measured by the luminescence spectrometer used here.

The iridium complex N-948 incorporated in PS or in AP200/19 upon excitation at 494 nm, emits strong phosphorescence at 665 nm (see Fig. 3). This emission is quenched when the membrane is exposed to oxygen (see dotted line in Fig. 3).

Table 1 shows the luminescence excitation and emission properties of the different sensing layers. In addition, table 1 also shows the luminescence quantum yield of the N-948 in solution and incorporated in PS and AP200/19. The luminescence quantum yields of the polystyrene films independent of the presence of the plasticizer *o*-

CPOE are similar (around 0.58 ± 0.05). Thus the use of a plasticizer to modify the physical properties of the polymeric sensing layer does not affect the luminescence efficiency. Nevertheless, the luminescence quantum yield of the N-948 incorporated in the nanostructured film is 0.20 ± 0.01 only; which is three times lower than that of the PS membranes. In solution it is 0.1 ± 0.01 , approximately two times lower than in AlOOH and six times lower compared to the polymeric matrix. In earlier publications, a lower luminescence quantum yield for polymeric membranes was shown compared to nanostructured films ^{10,11}. In this case, due to the high lipophilicity of N-948, the quantum yield of the dye solubilized within PS is higher than in AP200/19. This effect may be related to the improved solubilization of the dye in the polymer film compared to the AlOOH matrix and to the conformational freedom the OMC has in the solution compared to the nano-sized pores. Generally, an increased rigidity of the matrix contributes to a higher quantum yield by conserving the structure of the complex and its ligands.

The phosphorescence lifetime data of the oxygen-sensitive membranes in nitrogen atmosphere (τ_0 ; 0% O₂) are tabulated in Table 1. On the one hand, the N-948 incorporated into pure PS-membranes and membranes plasticized with *o*-CPOE shows generally a longer luminescence lifetime, τ_0 , than the AlOOH-sensing-films. This effect may be referred to the polymer environment, which provides a medium to the lipophilic dye where it is easily solubilized and has the necessary conformational freedom. On the other hand, the use of *o*-CPOE decreases the luminescence lifetime, τ_0 , and quenches the luminescence emission of the metal complex. The quenching of the dye by *o*-CPOE is well known¹⁰ and is observed again for the metal organic complex N-948.

In conclusion, N-948 is the first Ir complex in the literature with a luminescence emission at a wavelength higher than 650 nm, a quantum yield higher than 0.50 and an extremely long phosphorescence lifetime which has been used for developing oxygensensitive films.

3.3. Oxygen sensitive properties.

Luminescence quenching methods of analysis are based on the decrease in emission intensity in the presence of the quencher (oxygen), and are described by the Stern-Volmer equation (see equation 1).^{10,11, 12,14,,25}

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + k_{SV} p O_2 \tag{1}$$

where *I* is the luminescence intensity, τ is the decay time or the phosphorescence lifetime, the subscript "0" refers to the value in the absence of quencher, k_{SV} is the Stern-Volmer constants and pO_2 is the partial pressure of oxygen.

However, deviations have been observed, and these are often attributed to the heterogeneity of the medium in which the dye is dispersed. The heterogeneity is attributed to different types of oxygen quenching sites within the matrix.^{11,39} When two microdomains are expected, the experimental data can be fitted using a two-site model proposed by Demas and co-workers, and called the Demas' model (see equation 2)⁴⁰

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = \left[\frac{f_1}{1 + k_{SV,1}pO_2} + \frac{f_2}{1 + k_{SV,2}pO_2}\right]^{-1}$$
(2)

where f_i denotes the fractional contribution of the total luminescence emission from the luminophore located at site type *i* under unquenched conditions, which exhibit a discrete Stern-Volmer quenching constant given by $k_{SV,i}$.³⁹ Other model was proposed by Lehrer⁴¹ in which only one microenvironment is accessible to the quencher ($k_{SV,2}$ =0; see equation 3)

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = \left[\frac{f_0}{1 + k_{SV} p O_2} + (1 - f_0)\right]^{-1}$$

 $(\mathbf{3})$

where f_0 denotes the fraction of the total luminophore's population that is accessible to the quencher, and k_{SV} is the Stern-Volmer quenching constant which is associated with the accessible fraction of luminophores.

Fig. 4 shows the Stern-Volmer plots obtained in all the experiments (symbols) and the fit to the theoretical data obtained with Lehrer model (line) and Figure 5 shows the decay curves for PSOX membrane at different partial pressure of oxygen which were used to draw the SV plots based on lifetime measurements.

The experimental results cannot be explained by a linear relationship between oxygen pressure and emission intensity relative to the luminescence lifetime, thus a two site model has to be used to fit the experimental data. In addition, the fitting of the experimental data by using the Demas' model provides incorrect results (see Table 2), only Lehrer's model may be used to fit the experimental data. It means that the oxygensensitive membranes are heterogenic and/or dye aggregation effects occur. The heterogeneity of the nanostructured metal oxide supports has been pointed out previously^{11,32-34} and it should be the responsible of the experimental results of AP200/19 membranes: the dye is located in two different environments, one which can be quenched by oxygen and another where oxygen is not able to quench it or has not access. Dye aggregations effects are more frequent on polymer films providing similar results than using nanostructured metal oxides⁴². These hypotheses explain why the Lehrer's model may fit the experimental data.

The analysis of the experimental results shows that the Stern-Volmer constant, k_{SV} , of N-948 incorporated into AP200/19 is much higher than within the PS-matrix. This effect of the AP200/19 matrix may rather be traced back to the capillary forces and the permeation of oxygen through the nanostructured matrix than to the chemical environment of the pores. The metal oxide matrix is formed from agglomerated particles, where the nanopores are located inside while the macropores appear between agglomerated particles ¹¹. Since the capillary forces are high, the oxygen is quickly driven into the nanopores (pore diameter < 50 nm).¹¹ This structure was shown before to be responsible for the much higher sensitivity of different OMCs, Ru(II)- as well as a variety of iridium complexes (N-926, N-833 and N-837), to oxygen compared to the polystyrene matrix.

The results in Table 2 show, that using the plasticizer (*o*-CPOE) decreases the k_{SV} . *o*-CPOE not only decreases the luminescence lifetime, τ_0 (see section *Spectroscopic behavior of oxygen-sensitive material*), but even more, quenches the luminescence emission of the metal complex and thus reduces the fraction of the luminescent dye that is accessible for luminescence quenching by oxygen. In addition, an increase in the concentration of the *o*-CPOE goes along with a decreasing Stern-Volmer constant. This effect was similarly observed for other Ir complexes immobilized within PS.¹⁰

In Table 2, the Stern-Volmer constants derived from decay time (phosphorescence lifetime) measurements for the PS-films are shown only. The luminescence lifetime of N-948 incorporated into the AlOOH-membrane was too short to be accessible to the available instrumentation. In comparison, for N-948 incorporated into PS membranes, the Stern-Volmer constants derived from investigations of the luminescence intensity were very similar to those derived from investigations of the decay time whether a plasticizer was added or not (see Table 2). The luminescence lifetime SV plots coincided fully with the intensity SV plots (see Fig. 4).

In order to confirm the merits of N-948 as an oxygen-sensitive OMC, another Ircomplex with a high luminescence quantum yield and high lipophilicity was selected and immobilized within the same matrix (PS and AP200/19). This compound was N-926 (bis(2-phenylpyridinyl)-N,N,N,N-tetramethyl-(4,4'-diamine-2,2'-bipyridinyl) iridium (III) chloride).¹⁰. In comparison, N-948 shows a Stern-Volmer constant (18.2 ± 1.2 bar⁻¹) 20 times higher than the k_{SV} of N-926 in PS (1.20 ± 0.03 bar⁻¹) whereas the use of AP200/19 provides a k_{SV} of 33.5 ± 1.3 bar⁻¹ for N-948 which is 3 times lower than that of N-926 in AP200/19 (101.9 ± 11.6 bar⁻¹). The higher lipophilicity of N-948 seems to counteract the benefits of the rigid metal oxide medium in the pores from which N-926 can benefit. The higher lipophilicity of N-948, on the one hand, favors the solubility in the PS matrix and increases the k_{SV} . On the other hand the larger structure is most probably responsible for a lower penetration into the positively-charged nanopores of the AP200/19.

3.4. Reversibility, response time and long-term stability.

Fig. 6 shows the luminescence intensity of PSOX membranes which varies with the partial pressure of oxygen. The complete reversibility of the luminescence emission of the oxygen-sensitive films allows to monitor an increasing and decreasing pO_2 continuously. The physico-chemical quenching reaction is a reversible process. In addition, the oxygen-sensitive membranes show quick response times: the t₉₅ response time of the optodes are <2 s when changing from 10 vol.% pO₂ to 90 vol.% pO₂, and <4s when changing from 90 vol.% pO₂ to 10 vol.% pO₂.

Since their analytical performance (k_{SV}) did not change over 12 months storage under ambient conditions, the long-term stability of all the oxygen-sensitive membranes was considered to be sufficiently good for measurements in the gas phase (see figure 7).

Conclusions

The phosphorescent iridium-complex N-948 was investigated in view of its application in oxygen-sensitive chemical sensors. The organometallic complex was incorporated into a nanostructured metal oxide matrix as well as into a solvent polymeric polystyrene membrane and characterized in the gas phase for its response to oxygen. The films show a phosphorescence emission band at 665 nm which is quenched by oxygen. This emission band is excited at the wavelengths where the MLCT-transition occurs, at 495 nm. The luminescence quantum yield, Φ , of N-948 incorporated into a non-plasticized PS-film is 0.58, and a lifetime of the phosphorescence emission of 102 µs was determined. Thus, it is the first Ir complex in the literature with a luminescence emission at a wavelength higher than 650 nm, with a quantum yield higher than 0.50 and an extremely long phosphorescence lifetime which has been used for developing oxygen-sensitive films. The transparent oxygen-sensitive films show complete reversibility with short response times. Different from the PS-film, the nanostructured metal-oxide film increases the photostability of the compounds and resists to heat and γ irradiation during sterilization. The oxygen-sensitive membranes can be used in current solid-state opto-electronic monitoring devices.

Acknowledgment. The authors gratefully acknowledge the financial support of the Junta de Andalucía (Proyecto de Excelencia RNM-666 and contract with the Andalusian Agency of Water ref. 2243). Also, the authors are grateful to Ilford Imaging Switzerland GmbH (Switzerland) for supplying the metal oxide membranes.

Electronic supporting information (ESI). Photophysical data for the most relevant Ircomplexes and crystallographic information file (CIF) of N-948.

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| Name | wt.% PS | wt.% <i>o</i> - CPOE | wt.% dye | λ _{exc/em} (nm) | Φ^{a} | $\tau_0 \ (\mu s)^b$ |
|-----------------------|------------|-------------------------|-------------|-----------------------------|---------------------|----------------------|
| Solution ^c | - | - | - | 495/681 | 0.10 ± 0.05 | n.d. |
| PSOX | 98.6 | 0.0 | 1.4 | 494/665 | 0.57 ± 0.05 | 102 ± 1 |
| PS1XC | 90.0 | 8.7 | 1.4 | 494/665 | 0.58 ± 0.06 | 93 ± 1 |
| PS2XC | 81.6 | 17.0 | 1.4 | 494/665 | 0.61 ± 0.03 | 78 ± 1 |
| AlOOH ^d | - | - | - | 494/665 | 0.20 ± 0.01 | 22 ± 3 |

Table 1 Nomenclature and composition of the oxygen-sensitive membranes and the luminescence properties of N-948 in solution and incorporated in a solid support.

^aThe luminescence quantum yields were calculated according to reference 10 and the results are expressed as the average of three replicas \pm (*n*=3, *t*=4.30 (2*P* = 0.05).

^bThe lifetime (τ) was calculated in absence of oxygen, slit width_{exc/em}=10/10 nm, detector voltage=850V, t_d=0.01 ms, t_g=0.01 ms, total decay time=1s and number of cycles=100 and the results are expressed as the average of three replicas ± (*n*=3,

t=4.30 (2P = 0.05).

°1.5 mg L⁻¹ N-948 dissolved in dichloromethane. Slit width_{exc/em}=20/20 nm, detector voltage 600 V

^dThe AlOOH film was obtained by spin-coating of a solution of 1.5 mg L⁻¹ N-948 dissolved in chloroform.

Table 2 Stern-Volmer constant of N-948 incorporated into PS plasticized with and without *o*-CPOE and AP200/19 obtained by Demas' and Lehrer's models and using intensity and lifetime measurements (for $\lambda_{exc/em}$ see Table 1).

| | | | Dema | Lehrer's model | | | |
|-----------|-------|-----------------|-------------------------|----------------|---------------------------|-----------------|------------------------|
| | | f_{I} | $k_{SV,1} (bar^{-1})^a$ | f_2 | $k_{SV,2} (bar^{-1})^a$ | fo | $k_{SV}(bar^{-1})^{a}$ |
| Intensity | PS0X | 0.95 ± 0.07 | 19.4 ± 1.3 | 0.10 ± 0.05 | $\textbf{-0.02} \pm 0.03$ | 0.90 ± 0.05 | 18.2 ± 1.2 |
| | PS1XC | 0.94 ± 0.07 | 10.0 ± 1.3 | 0.10 ± 0.06 | $\textbf{-0.07} \pm 0.09$ | 0.89 ± 0.06 | 9.6 ± 1.2 |
| | PS2XC | 0.88 ± 0.10 | 7.8 ± 0.8 | 0.15 ± 0.09 | -0.04 ± 0.06 | 0.85 ± 0.08 | 7.6 ± 0.9 |
| | Alooh | 1.19 ± 0.29 | 52.1 ± 16.0 | 0.19 ± 0.08 | $\textbf{-0.03} \pm 0.11$ | 0.81 ± 0.11 | 33.5 ± 1.3 |
| Lifetime | PS0X | 0.96 ± 0.02 | 19.9 ± 1.6 | 0.04 ± 0.00 | -0.24 ± 0.53 | 0.94 ± 0.00 | 18.6 ± 0.9 |
| | PS1XC | 0.98 ± 0.11 | 10.2 ± 1.6 | 0.03 ± 0.01 | $\textbf{-0.07} \pm 0.07$ | 0.86 ± 0.01 | 10.1 ± 0.5 |
| | PS2XC | 0.98 ± 0.01 | 7.8 ± 0.4 | 0.04 ± 0.00 | $\textbf{-0.06} \pm 0.03$ | 0.82 ± 0.01 | 7.2 ± 0.3 |

^a The experimental results have been expressed as the average of 3 replicas \pm

(n=3, t=4.30 (2P = 0.05)).

Caption figures

Fig. 1 Crystal structure of N-948 complex.

Fig.2 Absorption (left, 1.4×10^{-4} M, black line) and emission (right, 1.4×10^{-6} M, grey line) spectra of N-948 in dichloromethane solution at 298K. Excitation wavelength for the emission spectrum was 460 nm.

Fig. 3 Phosphorescence excitation and emission spectra of N-948 incorporated in AP200/19. (---; dash-dot) excitation spectrum in absence of oxygen, (---; solid line) emission spectrum in absence of oxygen, (..., dot line) emission spectrum in presence of oxygen. (For the composition of the membrane see Table 1). $\lambda_{exc/em}$ =494/665 nm, slits width_{exc/em}= 10/10 nm, detector voltage 700 V; t_d = 120 µs, t_g = 5 ms.(RPI: relative phosphorescence intensity)

Fig. 4 Stern-Volmer plots of data for • PSOX, ■ PSIXC and ▲ PS2XC membranes (see Table 1 for their composition) from (a) intensity and (b) lifetime quenching data. Solid lines are the best-fit line using equation 3. $\lambda_{exc/em}$ =494/665 nm, slits width_{exc/em}= 10/10 nm, detector voltage 700 V; t_d = 120 µs, t_g = 5 ms.

Fig. 5 Phosphorescence decay curve of PSOX membranes in exposure on (—; solid line) O% O₂, (--; dash line) 4% O₂ and (…; dot line) 20 % O₂ (For the composition of the membrane see Table 1). $\lambda_{exc/em}$ =494/665 nm, slits width_{exc/em}= 10/10 nm, detector voltage 850 V; t_d = 0.01 ms, t_g = 0.01 ms, total decay time 1 ms and 100 cycles.(RPI: relative phosphorescence intensity)

Fig. 6 Reversibility and response time of the PSOX membrane. Upper case: Increase in percentage of O_2 along the time axis, t in s, at a constant flow rate of 200 mL gas min⁻¹. Lower case: Decrease in luminescence intensity measured at 665 nm with increasing O_2 percentage along the time axis in s.

Fig. 7 Variation of the K_{SV} calculated according Lehrer's model for PSOX during 12 months using intensity data. Similar results were obtained for AP200/19 sensing layer.

Fig. 1



Fig. 2



Fig. 3



Fig. 4







Fig. 6



Fig. 7

