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Application of Gold Complexes in the Development of Sensors for Volatile Organic Compounds

Asunción Luquin[1], César Elosúa[2], Elena Vergara[3], Juncal Estella[1], Elena Cerrada[3], Cándido Bariáin[2], Ignacio R. Matías[2], Julián Garrido[1] and *Mariano Laguna[3]

[1] Departamento de Química Aplicada, Universidad Pública de Navarra, Pamplona, 31006, Spain
[2] Departamento de Ingeniería Eléctrica y Electrónica, Universidad Pública de Navarra, Pamplona, 31006, Spain
[3] Instituto de Ciencia de Materiales de Aragón-CSIC, Universidad de Zaragoza, Zaragoza, 50009, Spain
* Mariano Laguna. Tel: 34 976 76 11 81, Fax: 34 976 76 11 87 E-mail: alaguna@unizar.es

Abstract

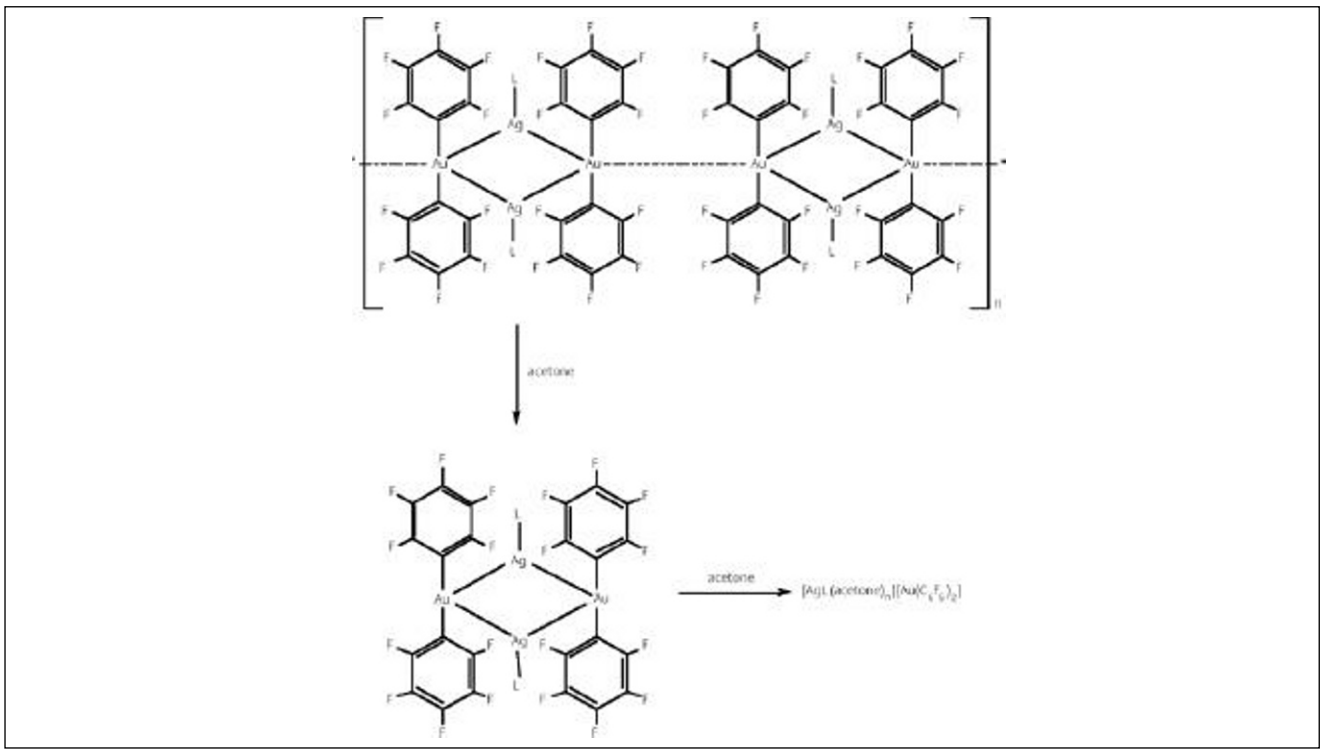
Two different kinds of sensors have been developed by using the same kind of vapochromic complexes. The vapochromic materials $[Au_2Ag_2(C_6F_5)_4L_2]_n$ have different colours depending on the ligand L. These materials change, reversibly, their optical properties, colour and fluorescence, in the presence of the vapours of volatile organic compounds (VOCs). For practical applications, two different ways of fixing the vapochromic material to the optical fibre have been used: the sol-gel technique and the electrostatic self-assembly method (ESA). With the first technique the sensors can even be used to detect VOCs in aqueous solutions, and using the second method it has been possible to develop nanosensors.

Introduction

Nowadays the detection of Volatile Organic Compounds (VOCs) is a very important objective for sensing technology, since there are many applications for this type of sensor (1). Among others, they have environmental applications, and can be used as electronic noses or in the chemical and food industry. We have focused our attention in vapochromic materials which can reversibly absorb VOC molecules, from the gas phase, with subsequent shift in their absorption spectrum. The first vapochromic material was described by Nagel (2) in 1988, and after that a large number of complexes with this property have been described (3,4), including different examples in gold chemistry.

It is well known that in the chemistry of gold it is possible to find a lot of complexes with interesting and useful properties. In our group we are especially interested in vapochromic gold complexes (4) and to develop this work we focused in vapochromic gold-silver organometallic complexes with the general formula $[Au_2Ag_2(C_6F_5)_4L_2]_n$ where L can be a N, O, P, C = C, C ≡ C donor ligand (5,6). These complexes were reported by some of us a long time ago and they have colours such as red, orange or yellow, depending on the ligand L. In the presence of VOC vapours such as acetone, methanol and ethanol, their colour changes to white or even colourless. One of the advantages of using these complexes is that by changing L we can have different complexes with slightly different properties suitable for the development of different kinds of sensors. Another advantage is that the crystal structure of the complex where L = C_4H_8S, C_3H_6O, C_6H_6 and $NCCH_3$ could be determined by X-ray diffraction (5,6). The unit cell consists of two gold and two silver atoms, each gold is bonded to the two silver atoms and to two pentafluorophenyl units, and each silver is bonded to the two gold atoms and to the ligand. There are also short contact distances between two gold atoms from different unit cells. In the presence of vapours of volatile organic compounds, the short gold-gold interactions are broken and if there are still more vapours the gold silver bonds are also broken giving a colourless material (see Scheme 1).

We describe here the preparation of optical fibre sensors because they have a lot of advantages over electronic ones (7). For example, they have a high electrical resistance, making this kind of sensor safe for use near high voltage equipment, they can be multiplexed effectively on a single fibre network, they are immune to electromagnetic interferences, including nuclear electromagnetic pulses, because there are no electrical currents flowing at the sensing point. They are small with respect to both size and in weight, and they are suitable for difficult environments. The sensors have been developed using two different ways of fixing the vapochromic material to the fibre optic, the sol-gel technique and the electrostatic self assembling method.



Scheme 1

Representative structure of complexes $[Au_2Ag_2(C_6F_5)_4(L)_2]_n$ and reaction with acetone

Experimental

General procedures

The general set-up of the optical fibre sensor consists in a light source, a sensor system and a detector (Figure 1), all of them joined by fibre optic. The light source employed depends on the way the sensor system is fixed to the optical fibre as discussed in the results and discussion section below.

To measure the vapochromic fluorescence characteristics, the emission spectra and the response of the sensor to different VOCs in terms of their absorbance spectra have been measured. To carry out this analysis the set-up employed was the one used for the sensor but this time a CCD Spectrometer PC2000 was connected in the place of the detector, a LED at 385 nm and a white light source to study the sensor absorbance spectra were connected in the place of the light source.

$[Au_2Ag_2(C_6F_5)_4(L)_2]_n$ L = phen(1), 2,2'-bipy(2) or py(3) were synthesized by following published methods (5).

Optical power measurements

The sensor system consists of a standard optical fibre. The vapochromic material is deposited on the optical fibre, at the end or somewhere in the middle, depending on the mode employed to develop the sensor. In the reflection mode, the vapochromic material is deposited exactly on the fibre end. The fibre was cut at the end with a Siemens S46999-M9-A8 precision fibre cleaver, the thickness is around 0.25 mm and the other end of the fibre is connected to a Y optical coupler 50:50. In the transmission mode a single mode fibre was tapered and the vapochromic material deposited on the thinner region of the resulting tapered fibre. Tapering of a fibre consists of pulling the fibre while it is being heated, in order to obtain a thin region in which light guiding conditions are different from those in the non-tapered regions. In this work, an Ericsson FSU 905 splicing unit was used. The fusion splicer is programmed in such a way that fusion currents are lower than those used in fibre splicing and fusion times are longer. In this case, the fibre was malleable, but not degraded by heat, and there was enough time to pull the fibre. Using this method, it is possible to obtain tapers with different parameter values, allowing a smaller region range to be covered with a variable refractive index material, thus obtaining a smaller sensor at a lower cost. In both cases the set-up was completed with an optical source to generate the interrogating signal and an optical detector to measure the modulated optical signal received. The sensor system was characterized at two interrogating LASER wavelengths 1310 and 1550 nm (modules 665R and 666R from Rifocs

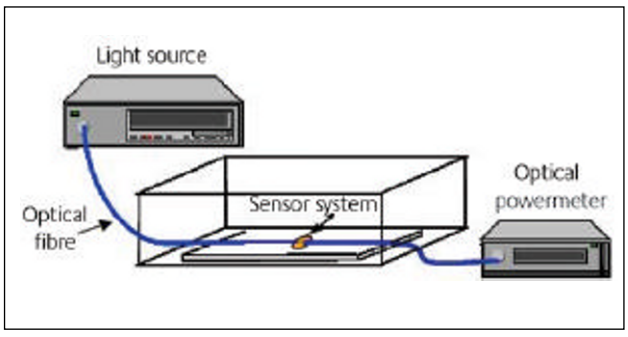


Figure 1

General set up of an optical fibre sensor

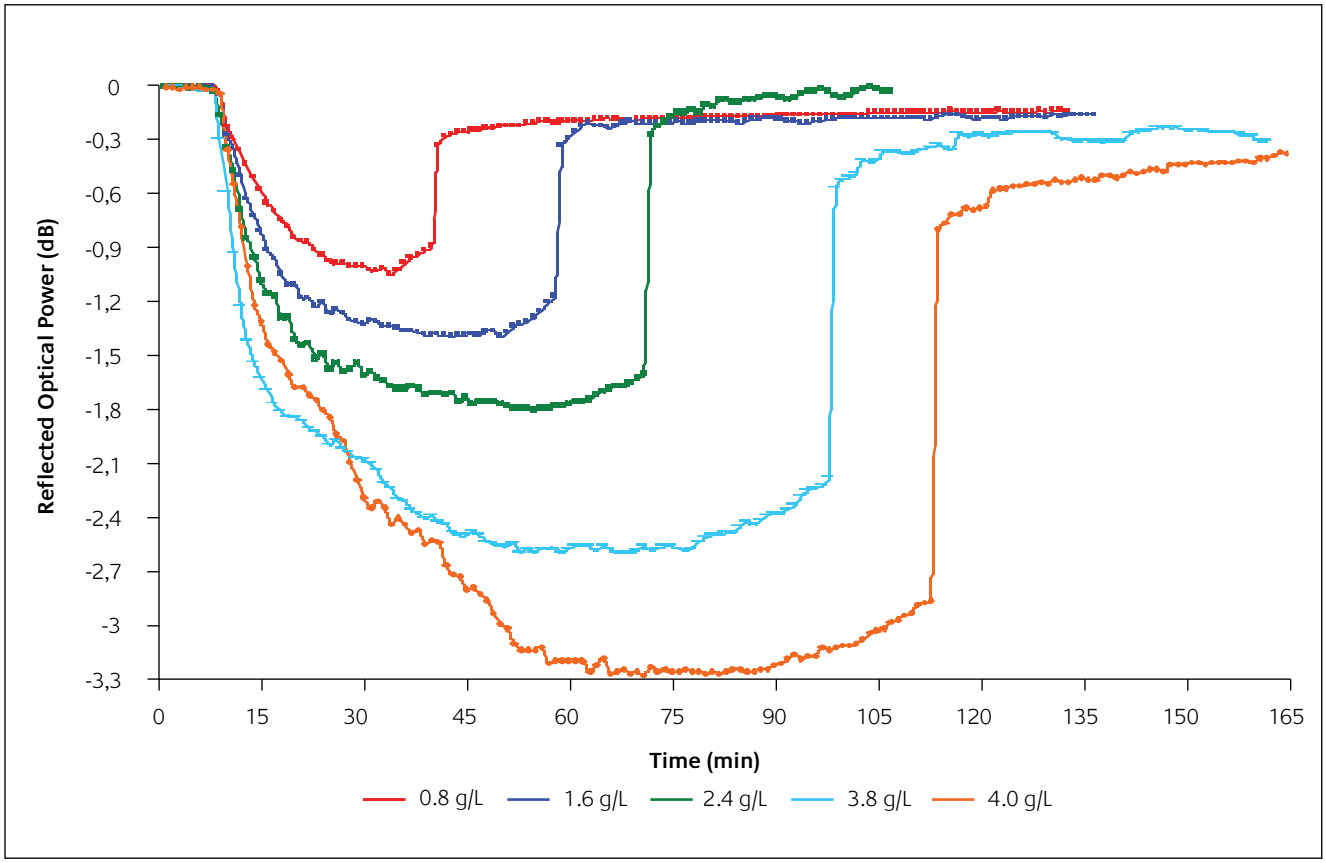


Figure 2

Behaviour of the sensor exposed to different acetone concentrations

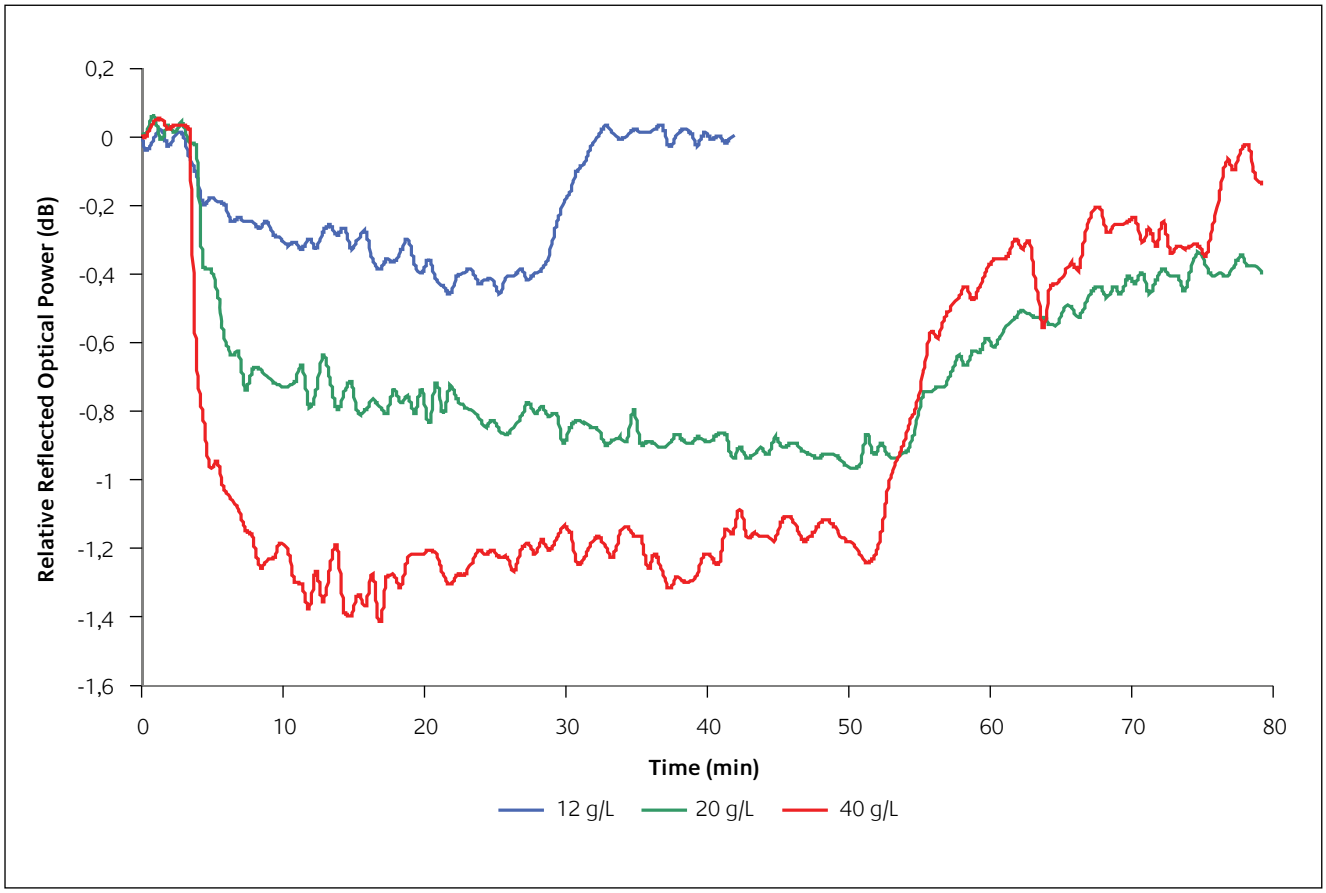


Figure 3

Behaviour of sensor submerged in water, at different acetone concentrations

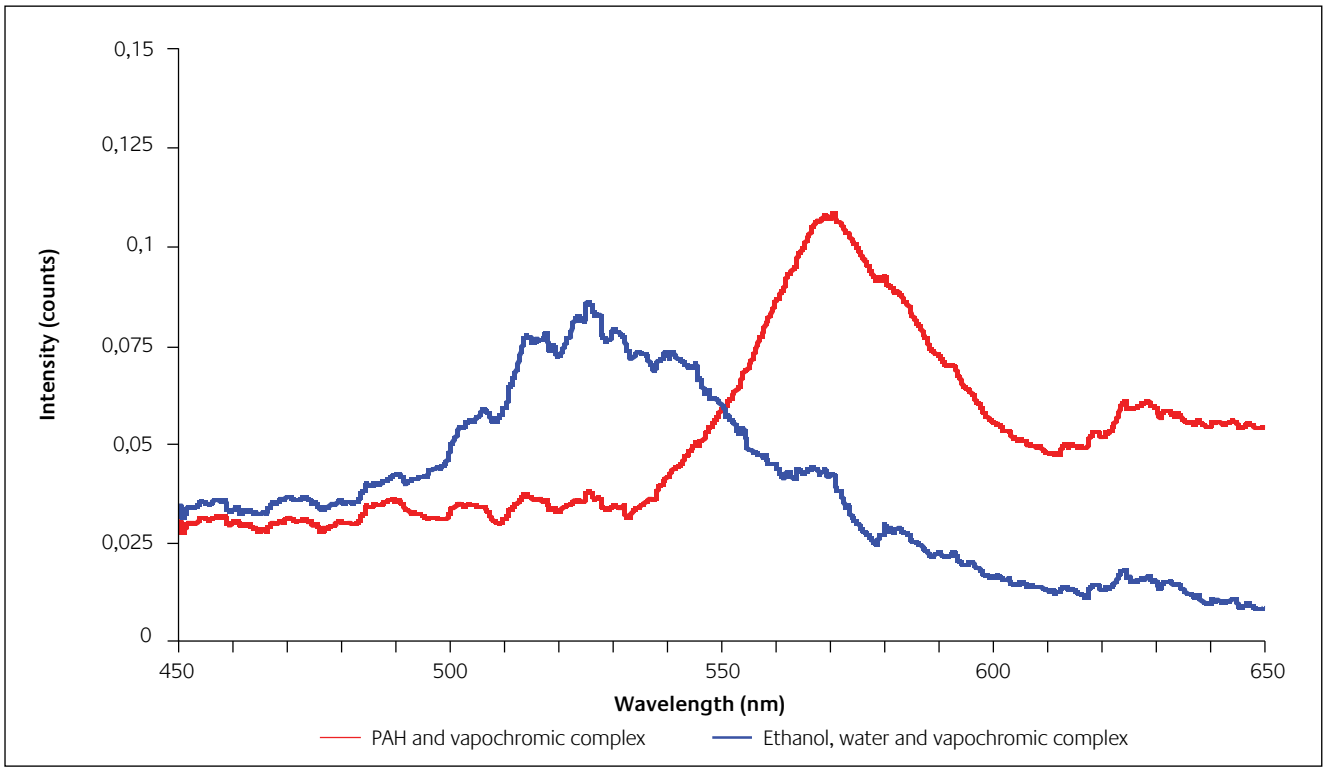


Figure 4
Fluorescence spectra when excited at 385 nm

Corporation, respectively) in the case of sensors developed by the sol-gel technique, and by a LED in the case of sensors made by the ESA method. At least five different concentrations of acetone, as VOC, were employed here. The photodetector was a 675RE, also from Rifocs Corporation. The fibre covered with the vapochromic material was placed inside a glass container that could be hermetically sealed.

Fibre optic sensors

The general set-up for the optical fibre sensors consists of a light source, a sensor system and a detector with all of them joined by a fibre optic (Figure 1). The light source was a LASER in the sensors developed by using the sol-gel method and an LED in sensors made using the ESA technique. The sensor system should be modified, at least, in one of its optical properties (colour, refractive index or fluorescence) when the monitored substance is in the surrounding environment.

Vapochromic material fixation to the fibre

The vapochromic material was fixed to the fibre using two different techniques, the sol-gel method, which allows the construction of sensors able to detect VOCs even in aqueous solution and by the ESA technique which is useful to develop nanosensors. It is important to notice that both kinds of sensors had been developed by using the same kind of complexes for the sensor system.

The sol-gel process consists of preparing a xerogel by mixing tetraethylorthosilicate (12 mmol, 669 µl), water (pH 4, adding HCl as required, 216 µl), ethanol (12 mmol) and a sufficient quantity of vapochromic complex to give a concentration of 10^{-4} M. After drying this mixture for two weeks, a viscous gel, containing the vapochromic material is formed, this gel is fluid enough to be deposited on the optical fibre. It dries to give a xerogel that is perfectly adhered to the fibre.

The ESA process consists of ionic monolayers doped with the vapochromic material, deposited at the end of a fibre optic. Firstly the fibre optic is cleaned and chemically treated to produce a charged surface and then the substrate is alternately dipped into solutions of polycation and polyanion to create a multilayer thin film. Polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) where used as polyelectrolytes.

Results and discussion

Polynuclear gold-silver complexes with general formula $[Au_2Ag_2(C_6F_5)_4L_2]_n$ where used to develop sensors by two different methods, the sol-gel technique and the electrostatic self-assembling method. These gold-silver complexes were chosen because their colours, which are red, yellow, orange, change to white or even colourless in the presence of VOC vapours. (Scheme1)

Sensors developed by using the sol-gel technique

The sol-gel process was used to fix the vapochromic material to the fibre optic because the resulting gel and the optical fibre have almost the same refractive index, thus avoiding signal loses by reflection. As previously discussed, the light sources employed in these sensors were commercially available lasers, and the wavelengths used were between 1310 and 1550 nm.

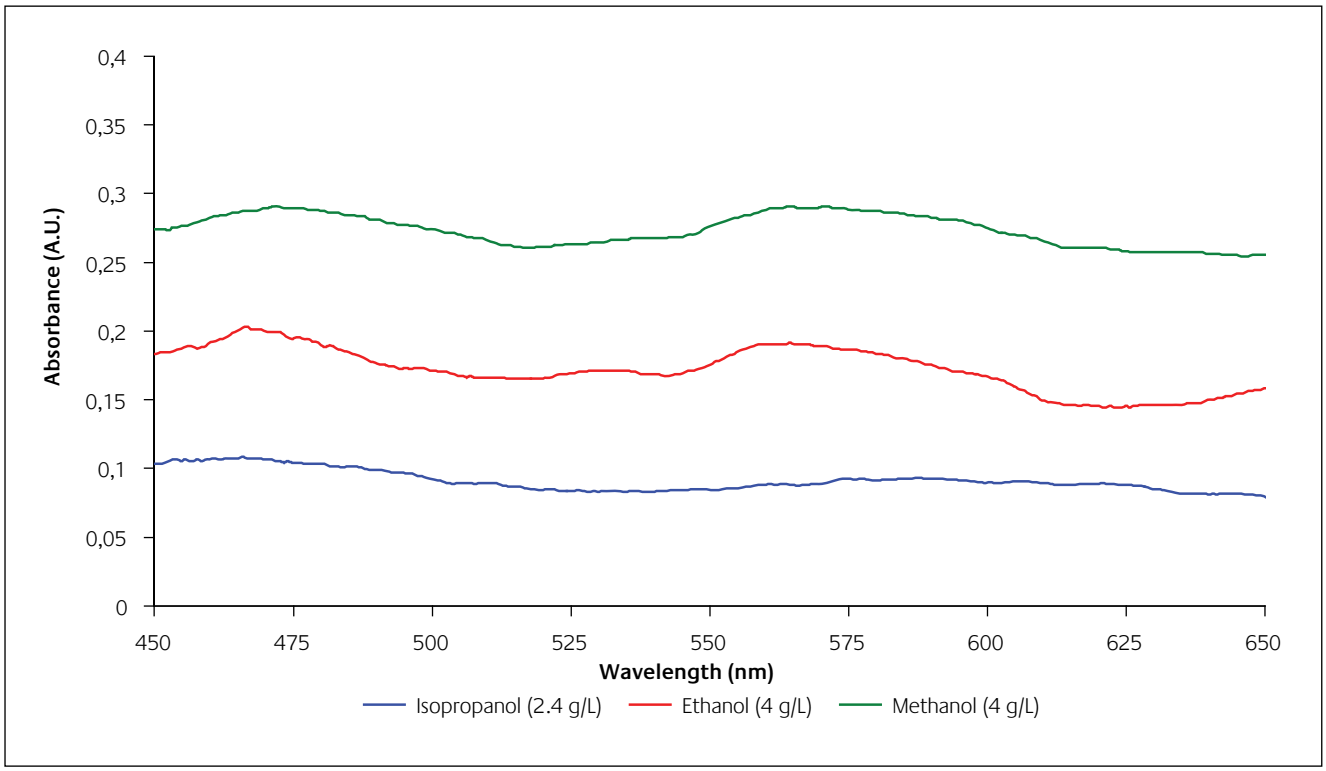


Figure 5

Absorbance spectra measured 40 minutes after exposure

The xerogel can be placed at the end of the optical fibre, giving a sensor in the reflection mode, or somewhere in the middle of the fibre, giving a transmission mode sensor but the general set-up is the same in both cases, the only difference is the place where the vapochromic material is deposited. In both cases the optical fibre should be prepared before the deposition of the vapochromic material. To develop sensors in the reflection mode, the optical fibre should be cut to obtain a smooth surface, without imperfections, because if the contact between the fibre and the sensing material is not perfect, inaccuracies will occur. Once the surface is as smooth as possible, the xerogel is deposited and it is allowed to dry. In the transmission mode sensors the optical fibre is stretched in order to make it narrow, this way, the vapochromic material, once deposited, is in contact with the core of the fibre and not with the cladding, in this tapered zone will be placed the gel and it will be allowed to dry.

Figures 2 and 3 show the results obtained with sol-gel sensors in the reflection mode. All the experiments were carried out with acetone as VOC. In Figure 2 it is possible to see how in the moment the VOC is added to the chamber the reflected optical power changes, and the change is bigger when the concentration of acetone is bigger, the biggest variation, around 3.3 dB is due to the biggest concentration of acetone added (4 g/L). When the optical power becomes stable, the chamber is opened to eliminate the vapours, and the response is almost immediate towards a value very similar to the initial one. In Figure 3 the same set-up was used, but this time the sensor was submerged into 20 mL of water. The behaviour is very similar, when the VOC is added to the water, the reflected optical power changes. When the sensor is taken out of the solution the reflected optical power goes towards the initial one, but this takes more time. This is probably due to the fact that in the surface of the sensor there are still water molecules and they can be doped with the VOC.

The results obtained with the sensor developed in the transmission mode are very similar to those observed in Figure 2. All the experiments were made in order to confirm that the technique for the construction of the sensor is viable, the calibration curve was obtained for the sensor where L = 2,2'-bipy (8).

Sensors developed using the Electrostatic Self Assembling Method (ESA)

The main advantages of the electrostatic self assembling method is its simplicity and reproducibility compared with other deposition techniques employed to develop optical fibre sensors such as sol-gel (9), dip coating (10) or Langmuir-Blodgett (11).

The ESA method was used to fix the vapochromic material to the optical fibre, and it consists of the deposition of ionic monolayers of polyelectrolytes onto the end of the optical fibre, so the sensor is made in the reflection mode. One of the electrolytes should be doped with the vapochromic material in order to build up a thin layer sensitive to the VOC vapours. The electrolytes chosen where polyallylamide hydrochloride (PAH) as polycation and polyacrylic acid (PAA) as polyanion. The vapochromic material was not water soluble, so it was decided to dissolve it in the minimum amount of ethanol and then water was added. This water solution of the vapochromic material was mixed with a water solution of PAH. This solution method for complexes not soluble in water has

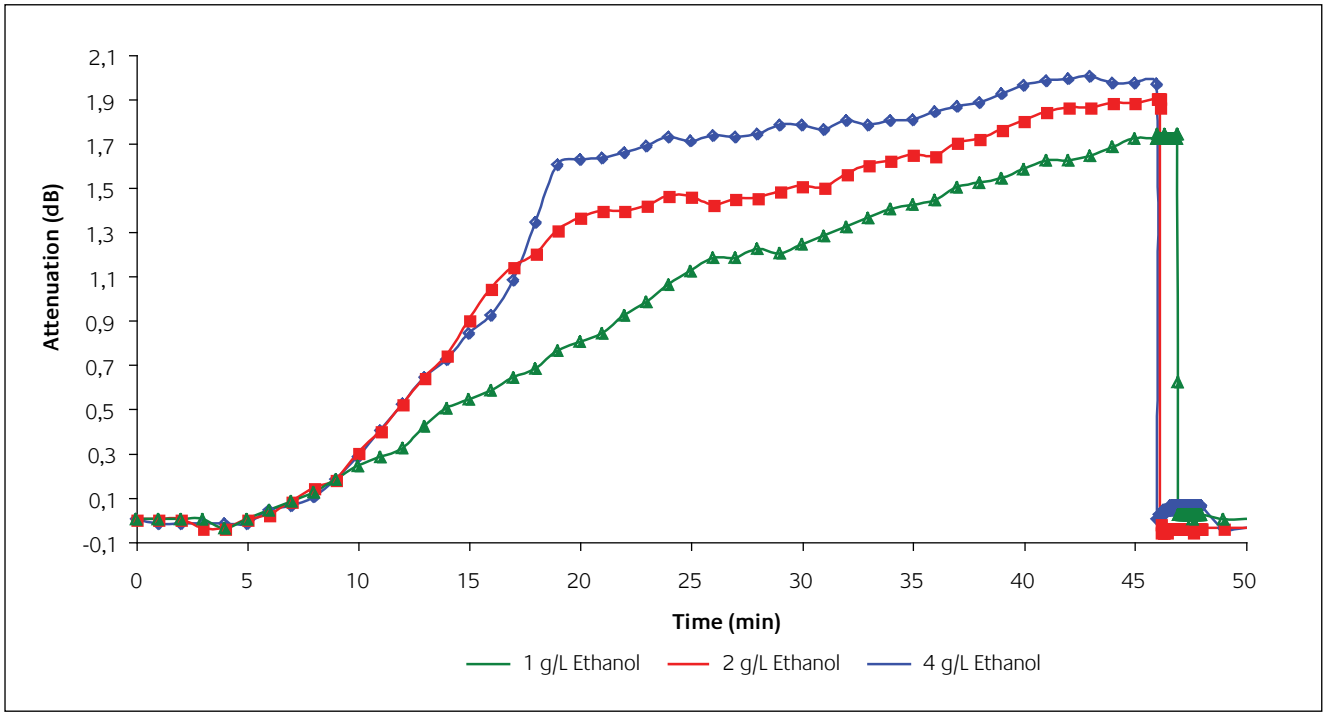


Figure 6

Response of the sensor to different ethanol concentrations

been described before (12). The polycation was doped with the vapochromic material because the PAH has a nitrogen atom which can act as a ligand, giving electrons to the silver and making dissolution of the complex easier. The pH of both polyelectrolyte solutions was set to 7 to avoid the destruction of the vapochromic material (13).

It is necessary to prepare the optical fibre to build-up the nanocavity, first of all it is necessary to create a charged surface, to do it the optical fibre was clean and treated with H_2SO_4 and H_2O_2 (3:1). Once the fibre was charged, it was submerged into the polycation solution doped with the vapochromic material and finally it was dipped into the polyanion solution. The process of dipping the fibre into the polyelectrolyte solution was repeated 25 times

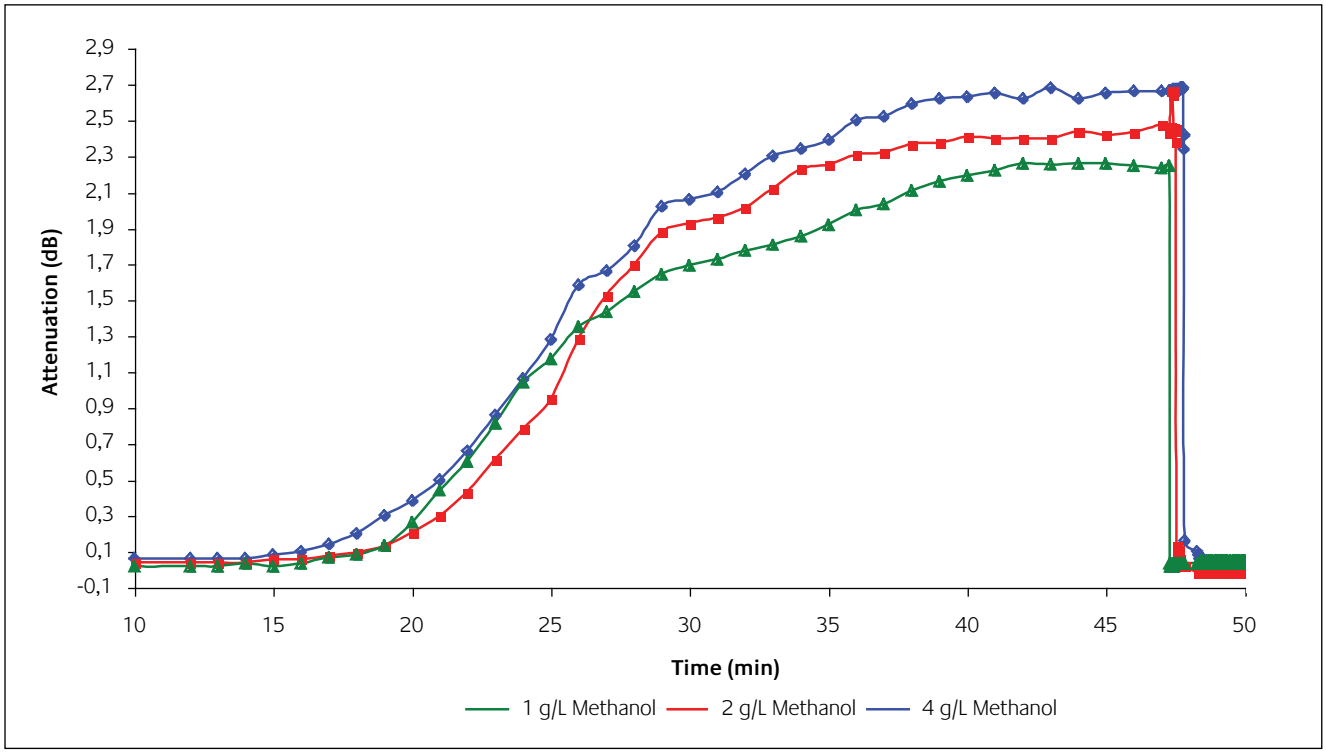


Figure 7

Sensor's response to different methanol concentrations

to give a thin layer consisting of 25 bilayers. The total thickness of the layer is important because depending on its nature the VOC will be absorbed with a characteristic speed (14). The thickness of each layer depends on the pH of the polycationic and polyanionic solution (13,15). As the deposition of the monolayers gives, from the optical point of view a homogeneous structure, it is possible to assume that the refractive index of the nanocavity is the same as that of the optical fibre (13, 16).

The light source used was an LED because the thickness of each layer was below the coherent length of the LED. The use of LEDs as light sources rather than LASERs allows the fabrication of smaller and cheaper sensors. The multilayer build-up at the end of the optical fibre allows operation as a homogeneous optical medium because the thickness of each monolayer is on the nanometer scale, as for the wavelength of the source used.

The powdered vapochromic material was excited with a light source at 385 nm, showing fluorescence at 575 nm. When the complex was dissolved first in ethanol and then in water, the colour and the fluorescence of the powders were maintained (Figure 4) but when the aqueous PAH solution was added to the solution of the vapochromic material in ethanol, the colour was lost and the emission peak, when excited at 385 nm, moved to 525 nm (Figure 4). These investigations indicated whether or not the vapochromic complex had doped the interferometric cavity properly. All these results mean that there is an interaction between the polycation and the vapochromic material, and as the mixture of the vapochromic material dissolved in ethanol and water and mixed with PAH is still fluorescent, it is concluded that the vapochromic complex was not destroyed by the acidic nature of the PAH solution. A valley in the absorbance spectra of the sensor around 530 nm could be further evidence that the vapochromic material is doping the interferometric structure.

The response of the nanocavity to ethanol, methanol and isopropanol, is shown in Figure 5. All of them show valleys in amplitude around 525 nm, near the fluorescence emission of the vapochromic compound dissolved in the polycation, meaning that the vapochromic compound is doping the cavity. The ethanol and methanol graphs are quite similar in shape, but the ethanol curve has a smaller amplitude. The spectrum for isopropanol has a lower amplitude and is almost flat, and this makes it easy to distinguish between isopropanol and the other two alcohols either by using the amplitude or the shape of the spectra, but to discriminate between methanol and ethanol is more difficult. To do this only the amplitude of the spectra can be used. This system has a high degree of flexibility and can be used over a wide region of the spectrum.

The VOC vapours were introduced into the chamber containing the sensor and the absorption process began around 30 minutes later. This time between the VOC addition and the adsorption process (longer than the time shown in other VOC sensors (17)) could be due to a number of factors such as the sensor curing process, the time it takes for the reaction between the VOC and the complex or the doping process, but it is mainly due to the time it takes for the VOC to get vaporised and to saturate the inside atmosphere. The influence of each of these factors response time is being studied and will be demonstrated in subsequent work. The reflected optical power changes when the VOC vapours are added to the chamber, but as it was shown in the sensors developed using the sol-gel technique, it reaches a certain

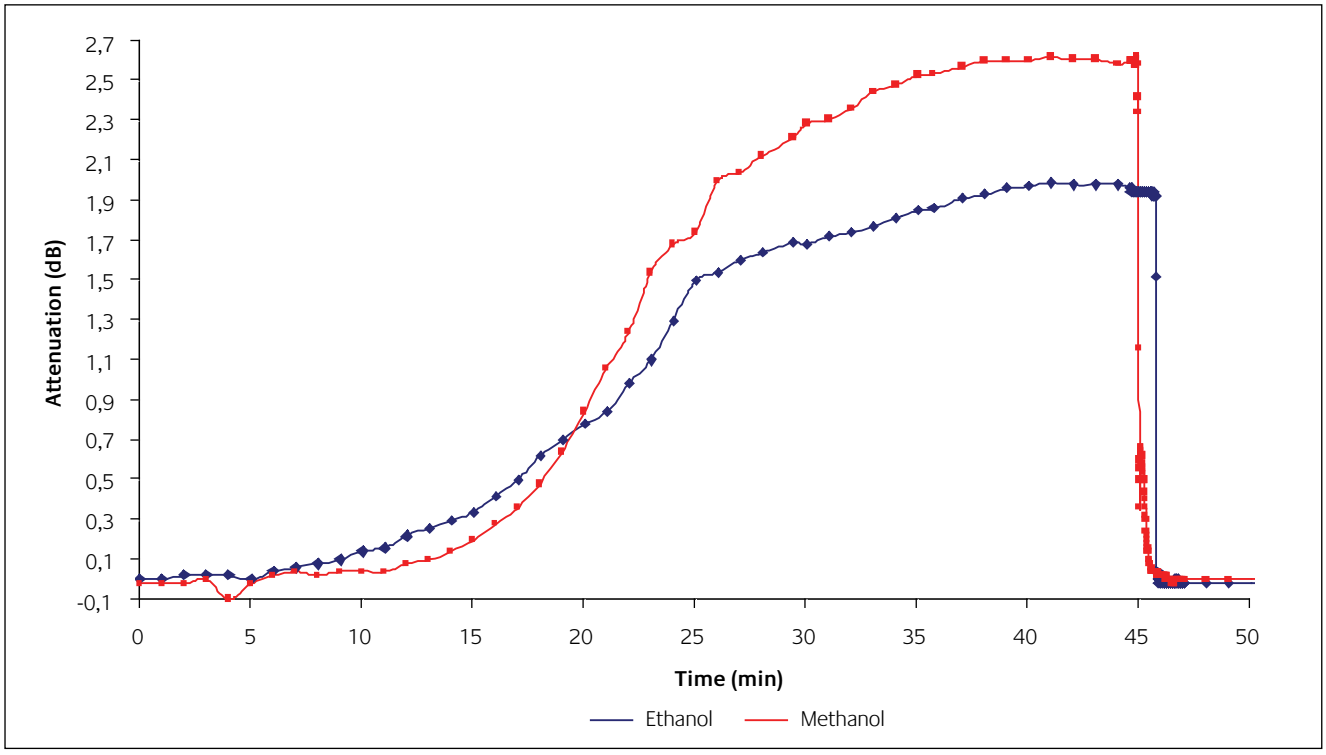


Figure 8

Comparison between the sensor response for the same ethanol and methanol concentrations (86 mmol/L)

stable value, and when the chamber is opened to eliminate the vapours the optical power recovers its original value. Different concentrations of ethanol (1 g/L, 2 g/L and 4 g/L) and methanol (1 g/L, 2 g/L and 4 g/L) where studied, and the response of the sensor to the different concentrations of ethanol and methanol are indicated in Figures 6 and 7 respectively. It is possible to see how the optical power does not differ much between them, only 0.3 dB for the ethanol and 0.4 dB for the methanol. The main difference between the measures is the time response. With smaller concentrations, the reflected optical power begins to increase later and the time needed to become stable is longer. This behaviour gives, at least, two possible signal processing methods to distinguish among the concentrations, either registering the time that the sensor takes to get to its higher level, or measuring the reflected optical power at one certain time since the vapour is introduced into the chamber.

The possibility of discrimination between fixed concentrations of ethanol and methanol vapours has been studied. The objective was to demonstrate that it is possible to discriminate between the two alcohols and show whether the response is repetitive or not. The experiment depicted in Figure 8 was carried out as explained before and it was made twice. The results show that the experiment is reproducible and it is possible to distinguish between these alcohols. This sensor has been used inside the laboratory for more than 7 months, and no variation in its behaviour or degradation of the doped nanocavity was observed.

These results confirm that the method used to develop the sensor is viable. Further work to attempt a calibration curve, in order to better compare the sensitivity of the sensor to different VOCs is currently in progress, as well as the study of the behaviour of the sensor when exposed to different concentrations of a number of VOCs.

Conclusions

The successful use of complexes of general formulae $[Au_2Ag_2(C_6F_5)_4(L)_2]_n$ as sensor systems is reported. They can be used in different kinds of sensors, for example those prepared using the sol-gel technique, which can detect VOCs even in solution, or by the ESA method which gives nanosensors.

The sensors developed using the sol-gel technique are very stable, and they have been used continuously for more than a year and are still operational; they are independent of the ambient conditions and are able to work even in aqueous solution. Since this sensor is small, it can be placed at any location. Its low cost, easy implementation and the possibility of multiplexing into either a telecommunication or a sensor network make it suitable for use in the petrochemical and chemical industries.

VOC sensors have also been developed using the ESA technique. These sensors can detect some VOCs and determine their concentrations, and offer high reproducibility and very efficient use of the vapochromic complex, and further investigations are likely to lead to improvements. This method permits the use of LEDs instead of LASERs, and this change in the light source allows the reduction in the size of the sensor and in its price.

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About the authors

Asunción Luquin

César Elosúa

Elena Vergara

Elena Cerrada

Cándido Bariain

Ignacio R Matías

Julián Garrido

Mariano Laguna

There are three groups involved in this work. Julián Garrido, Asunción Luquin and Juncal Estella are working at the Applied Chemistry Department at the Public University of Navarra, dealing with the synthesis and characterization of xerogels suitable for the development of optical fibre sensors. Cándido Bariáin, Ignacio R. Matías and César Elosúa are working at the Electrical and Electronic Engineering Department at the Public University of Navarra. They are developing optical fibre sensors and Mariano Laguna, Elena Cerrada and Elena Vergara are working at the Institute of Material Science, CSIC in Zaragoza, synthesizing materials suitable for use in these sensors.

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