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# New preparation of gold–silver complexes and optical fibre environmental sensors based on vapochromic $[Au_2Ag_2(C_6F_5)_4(phen)_2]_n$

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**Complexes $[Au_2Ag_2(C_6F_5)_4L_2]_n$, where $L = 1$,10-phenanthroline (phen), 2,2′-bipyridine (bipy) or tetrahydrothiophene (tht), have been synthesized by reaction of $NBu_4[Au(C_6F_5)_2]$ with $Ag(SO_3CF_3)$, and the addition of phen or bipy thereafter, or with $[Ag(SO_3CF_3)(tht)]$. The organometallic vapochromic material $[Au_2Ag_2(C_6F_5)_4(phen)_2]_n$ is isolated as a powder that is able to detect volatile organic compounds such as acetone even in an aqueous solution. The colour of this vapochromic material changes from bright yellow to white in the presence of different donor solvents such as acetone, methanol or ethanol. For the practical construction of an optical fibre sensor, a sol-gel doped with the vapochromic complex was deposited onto one end of a monomode fibre connected to a coupler. The behaviour of the material was studied at different wavelengths and concentrations of acetone vapours and acetone–water solutions. Changes were detected up to 4 dB in the reflected optical power. Copyright © 2005 John Wiley & Sons, Ltd.**

**KEYWORDS:** environmental sensors; optical fibre; vapochromism; gold; organometallic

## INTRODUCTION

Currently, there is an increasing interest in developing vapochromic materials that are able to sorb solvent molecules reversibly from the gas phase with subsequent modification of the absorption spectrum. Those materials are useful in the development of optical fibre sensors for vapour organic compound (VOC) detection.[1] Optical fibre sensors[2,3] have many advantages over conventional ones, such as immunity to electromagnetic interference, passive behaviour, the potential to use multiplexation techniques, low weight and small size. In addition, there are many fields where these kinds of sensors can be used, such as environmental applications, electronic noses or in the chemical industry.[4–6] The first vapochromic material, described by Nagel[7,8] in 1987, was an organometallic palladium–platinum complex. Mann *et al.*[9–18] reported additional examples in the chemistry of palladium and platinum, and also their use in the construction of some sensors and LEDs. Recently we reported the preparation and application in an optical fibre sensor of a novel organometallic vapochromic material, $[Au\{PPh_2C(CSSAuC_6F_5)PPh_2Me\}_2]ClO_4$,[19–22] that changes from black to orange in the presence of VOCs. Other researchers, including Eisenberg,[23–25] Laguna-Fackler,[26–29] Leznoff,[30] van Kotten,[31,32] Kabata[33] and Kato,[34] among others,[35–42] have described organometallic and coordination complexes that change colour or luminescent properties by reaction with selected VOCs. Although they have been suggested as possible candidates for VOC sensors, no devices were fabricated as proof, mainly because either the response to the volatiles is slow or the changes are not reversible.

Continuing our studies into these kinds of complexes[19–22] and looking for new organometallic complexes with vapochromic behaviour, some of us reported gold–silver

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organometallic complexes[43–46] with the general formula $[Au_2Ag_2(C_6F_5)_4L_2]_n$. Such complexes are coloured red, orange or yellow, depending on the ligand L, and they lose their colour completely on dissolution in solvents such as acetone, methanol or ethanol. In this paper we describe a novel synthesis of $[Au_2Ag_2(C_6F_5)_4L_2]_n$, where L = 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy) or tetrahydrothiophene (tht), and an optical fibre acetone sensor based on $[Au_2Ag_2(C_6F_5)_4(phen)_2]_n$. The new optical fibre sensor reported here, based on $[Au_2Ag_2(C_6F_5)_4(phen)_2]_n$, is able to detect acetone not only in the gas phase but also in water solution.

## EXPERIMENTAL

### General procedures

Infrared spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrophotometer over the range 4000–350 $cm^{-1}$ using Nujol mulls between polyethylene sheets, or using a Perkin-Elmer Universal ATR that samples over the range 4000–650 $cm^{-1}$. The mass spectra were recorded by matrix-assisted laser desorption/ionization (MALDI) in a MALDI micro MX de Waters without a matrix. Carbon, hydrogen and nitrogen analyses were performed with a Perkin-Elmer 2400 microanalyser. The weight experiments were made in a Mettler MX5.

### Materials

Complexes $NBu_4[Au(C_6F_5)_2]$,[47] $Ag(SO_3CF_3)$[48] and $[Ag(SO_3CF_3)(tht)]$[48] were prepared as described; 1,10-phenanthroline and tetraethoxysilane were commercially available from Aldrich and were used as received; and $[Au_2Ag_2(C_6F_5)_4L_2]_n$ was prepared by a safe modification of a described procedure,[43,44] using $Ag(SO_3CF_3)$ instead of $Ag(ClO_4)$.

### Preparation of $[Au_2Ag_2(C_6F_5)_4(L)_2]_n$
### (L = phen(1) or bipy(2))

To a dichloromethane solution (30 ml) of $NBu_4[Au(C_6F_5)_2]$ (0.193 g, 0.25 mmol), 0.25 mmol of $Ag(SO_3CF_3)$ (0.064 g) was added and the mixture was stirred for 45 min to form a yellow solution containing some yellow powder in suspension. Then, 1,10-phenanthroline monohydrate (0.049 g, 0.25 mmol) or 2,2′-bipyridine (0.039 g, 0.25 mmol) was added and an abundant yellow precipitate immediately appeared. After 30 min the solid was filtered off and washed with 2 × 5 ml of dichloromethane. Yield: **1**, 0.167 g, 82%; **2**, 0,159 g, 81%. Analysis of complex **1**, found: 35.3% C, 1.1% H, 3.5% N; $C_{48}H_{16}Ag_2Au_2F_{10}N_4$ requires 35.2% C, 1.0% H, 3.4% N. IR: $\nu(C_6F_5)$ 1050 (s,br), 965 (vs) and 784 (s) $cm^{-1}$; $\nu$(phen) 1632 (m) and 844 (s) $cm^{-1}$. MS: MALDI (%) 1081 (35) $[AuAg_2(C_6F_5)_2(phen)_2]^+$; 925 (2) $[AuAg_2(C_6F_5)_2(phen)]^+$; 807 (52) $[AuAg(C_6F_5)(phen)_2]^+$; 711 (100) $[Au(C_6F_5)_2(phen)]^+$, Analysis of complex **2**, found: 33.4% C, 1.1% H, 3.6% N; $C_{44}H_{16}Ag_2Au_2F_{10}N_4$ requires 33.2% C, 1.0% H, 3.5% N. IR: $\nu(C_6F_5)$ 1049 (s,br), 965 (vs) and 785 (s) $cm^{-1}$; $\nu$(bipy) 1592 (m) and 754 (vs) $cm^{-1}$. MS: MALDI (%) 1057 (39) $[AuAg_2(C_6F_5)_2(bipy)_2]^+$; 901 (3) $[AuAg_2(C_6F_5)_2(bipy)]^+$; 783 (47) $[AuAg(C_6F_5)(bipy)_2]^+$; 687 (100) $[Au(C_6F_5)_2(bipy)]^+$.

### Preparation of $[Au_2Ag_2(C_6F_5)_4(tht)_2]_n$ (3)

To a dichloromethane solution (30 ml) of $NBu_4[Au(C_6F_5)_2]$ (0.193 g. 0.25 mmol), 0.25 mmol of $[Ag(SO_3CF_3)(tht)]$ (0.086 g) was added and the mixture was stirred for 1 h. During this time the orange precipitate formed was filtered off and washed with 2 × 5 ml of dichloromethane (0.140 g, 77%). Complex **3**, found: 26.3% C, 1.2% H, 4.6% S; $C_{32}H_{16}Ag_2Au_2F_{20}S_2$ requires 26.4% C, 1.1% H, 4.4% S. IR: $\nu(C_6F_5)$ 1071 (sh), 1061 (vs), 969 (vs) and 786 (s) $cm^{-1}$. MS: MALDI (%) 1011 (21) $[Au_2Ag(C_6F_5)_2(tht)_2]^+$; 921 (15) $[AuAg_2(C_6F_5)_2(tht)_2]^+$; 833 (2) $[AuAg_2(C_6F_5)_2(tht)]^+$; 647 (100) $[AuAg(C_6F_5)(tht)_2]^+$; 619 (76) $[Au(C_6F_5)_2(tht)]^+$.

### Mass gain experiments

A 2.076562 g amount of $[Au_2Ag_2(C_6F_5)_4(phen)_2]_n$ (**1**) was placed in the presence of a saturated atmosphere of acetone for 60 s and thereafter was weighed. The mass increased because of the retention of acetone molecules, which then were lost over for a period of 360 s, and the mass gain/mass loss experiments were repeated ten times to establish the reproducibility. Three of these experiments are shown in Fig. 3 below and the other seven cycles are exactly the same. In other experiments 2.007534 g of complex **1** were placed in the presence of a saturated atmosphere of acetone for 30 s or for 1, 3, 5, 10, 20 and 30 min and then weighed (see Fig. 4 below) (30 s, 2.009433 g; 1 min, 2.010545 g; 3 min, 2.012302 g; 5 min, 2.012896 g; 10 min, 2.013745 g; 20 min, 2.014344 g; 30 min, 2.014560 g).

### Vapochromic material fixation to the fibre

The optical fibre employed was a standard 1.3 μm monomode fibre (core and cladding diameters of 9.4 and 125 μm, respectively). The optical sources used were two standard telecommunication windows (1310 nm and 1550 nm). The sensor system is introduced inside a cylindrical chamber 11.3 cm in diameter and 2 cm high (200 ml volume).

A sol-gel process was used to fix the vapochromic material to the optical fibre because the resulting gel and the optical fibre have the same refractive index, avoiding loss by reflection. A xerogel was prepared by mixing tetraethoxysilane (12 mmol, 669 μl), water (pH 4, adding HCl as required, 216 μl), a quantity of vapochromic complex to give a concentration of $10^{-4}$ M and ethanol (12 mmol). After drying this mixture for 2 weeks, a viscous gel containing the vapochromic material is formed. This gel is fluid enough to be deposited over the end of the optical fibre. It dries to give a xerogel that has adhered perfectly to the fibre.

### Optical power measurements

The sensor system consists of a standard single-mode optical fibre pigtail that ends cleaved with a Fujikara CT-03 precision

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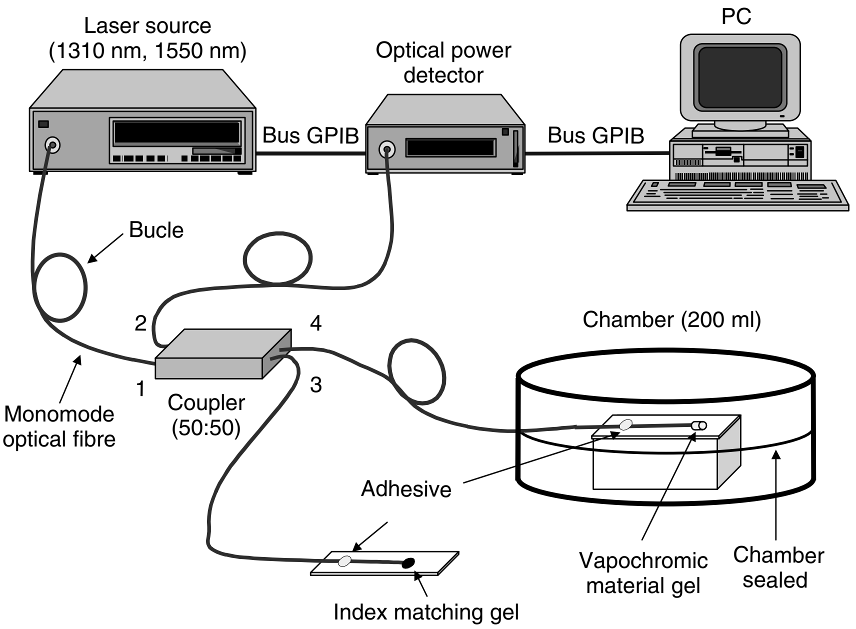


**Figure 1.** Optical fibre VOC structure. Exposure of the sol–gel vapochromic material to the vapour of acetone inside the container produces variations in the optical power output.

fibre.[6,22] Once the fibre is prepared, the vapochromic material is deposited exactly on one of the fibre ends; the thickness is around 0.25 mm. The other end of the fibre is connected to a Y optical coupler 50 : 50, i.e. the VOC sensor works in reflective mode. The set-up was completed with a Rifocs module optical source to generate the interrogating signal and an optical detector to measure the modulated optical signal received (Fig. 1).

The sensor system was characterized at two interrogating wavelengths 1310 and 1550 nm (modules 665R and 666R from Rifocs Corporation, respectively) and for at least five different concentrations of acetone for the VOC 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. The optical fibre was introduced into the container through a small orifice that was then sealed with silicone.

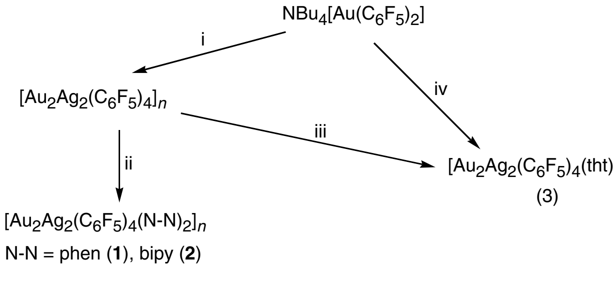
Acetone is introduced into this chamber by adding 0.1, 0.4, 0.7, 0.9 or 1 ml, representing concentrations of $6.81 \times 10^{-3}$, $2.72 \times 10^{-2}$, $4.77 \times 10^{-2}$, $6.13 \times 10^{-2}$ and $6.81 \times 10^{-2}$ mol $l^{-1}$. In the experiments to detect acetone in solution, 20 ml of a water solution containing 3, 5 or 10 ml of acetone was added to the chamber. The sensor was covered with those solutions.

The laser light comes through the optical fibre and is guided through the vapochromic material, which changes colour when exposed to VOC vapours. Then, the refractive index and the reflected optical power of the vapochromic material change. The modified optical power is guided to the detector (Fig. 1).

## RESULTS AND DISCUSSION

Polynuclear silver–gold complexes of general formula $[Au_2Ag_2(C_6F_5)_4L_2]_n$ (L = pyridine, 2,2′-bipyridine, 1,10-phenanthroline, benzene, tetrahydrothiophene and others)[43–46] are yellow, orange or red-coloured solids that give colourless solutions in the presence of coordinating solvents such as acetone, methanol or ethanol. They were made by equimolecular reaction of $NBu_4[Au(C_6F_5)_2]$ with $Ag(ClO_4)$ followed by addition of the corresponding ligand. The use of $Ag(ClO_4)$ presents serious safety problems and must be used in small quantities and handled with care, thus precluding its use for technical purposes.

For this reason, we replaced $Ag(ClO_4)$ with $Ag(SO_3CF_3)$, which reacts with $NBu_4[Au(C_6F_5)_2]$ to give a yellow solution containing a small yellow precipitate (Process i, Scheme 1). After addition of 1,10-phenanthroline or 2,2′-bipyridine, complex $[Au_2Ag_2(C_6F_5)_4(phen)_2]_n$ (**1**) or $[Au_2Ag_2(C_6F_5)_4(bipy)_2]_n$



(i) $[AgSO_3CF_3]$; (ii) phen or bipy; (iii) tht; (iv) $[Ag(SO_3CF_3)(tht)]$

**Scheme 1.**

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(**2**) precipitates as a yellow power in high yield (Process ii, Scheme 1). Complex $[Au_2Ag_2(C_6F_5)_4(tht)_2]_n$ (**3**) has been prepared either by addition of tetrahydrothiophene to the latter solution (Process iii, Scheme 1) or by reaction of $NBu_4[Au(C_6F_5)_2]$ with $[Ag(SO_3CF_3)(tht)]$, which represent an easier way to prepare such complexes by adding the stoichiometric quantities of tetrahydrothiophene (Process iv, Scheme 1). Complexes **1**–**3** have IR spectra and elemental analyses identical to those obtained using $Ag(ClO_4)$.[43,44]

Crystal structures of the complexes containing tetrahydrothiophene,[43,44] benzene[44] and acetone[46] have been reported and in all cases they show a tetranuclear structure (Fig. 2a) with two gold and two silver centres connected by gold–gold contacts. Each gold atom bears two pentachlorophenyl groups and each silver atom is bonded to one ligand (tht, benzene or acetone); the complexes are linear polymers across aurophilic interactions of ~3.0 Å, which is why we propose a similar structure for complex $[Au_2Ag_2(C_6F_5)_4L_2]_n$ (L = 1,10-phenantroline (**1**), 2,2′-bipyridine (**2**)), with the bidentate ligand bonded to the silver centres (Fig. 2b for phenanthroline).

All reported complexes are soluble in acetone, affording a colourless solution. It is known that the change of colour[43–46] is due to cleavage of the gold–gold contacts between two different metallacycles to give tetranuclear structures. The total loss of colour is due to the rupture of the Ag–Au bonds, as shown in Scheme 2. It is possible to confirm by IR spectroscopy that complexes **1**–**3** are able to add acetone when exposed to acetone vapours. The IR spectra of these products exposed to acetone vapours show bands at 1712 (w) and 1690 (sh) $cm^{-1}$ for complex **1**, at 1713 (w) $cm^{-1}$ for complex **2** and at 1709 (vw) $cm^{-1}$ for complex **3** compared with free acetone,[49,50] which shows $\nu_s$ (CO) at 1718 $cm^{-1}$. These data point to some degree of interaction of acetone with the complex, although they are not enough to indicate a bond with silver centres.

In this work we have selected the complex with 1,10-phenanthroline (**1**) to develop an organic vapour sensor for two reasons. First, this gold–silver complex shows more stability due to the bidentate behaviour of the ligand. Looking for some applicability of these types of complexes, we need to select stable vapochromic derivatives. Second, it adsorbs acetone more easily that the other complexes prepared in this work. Complex $[Au_2Ag_2(C_6F_5)_4(phen)_2]_n$ (**1**) reversibly changes colour at least ten times without decomposition after adding 5 ml of acetone and recovering the initial complex by vacuum evaporation of the solvent.

A study of the mass variation of complex **1** when exposed to acetone vapours is shown in Fig. 3. There is a mass increase in the presence of acetone vapours and then a gradual mass loss in the absence of these vapours, with the rate of acquisition being higher than the loss. In 60 s it adsorbs up to 100.15%, which is a very small but noticeable quantity of acetone, but it takes 6 min to lose all the acetone. A second exposure to acetone again shows an increase of weight up to the same quantity and the complex can perform these absorptions and

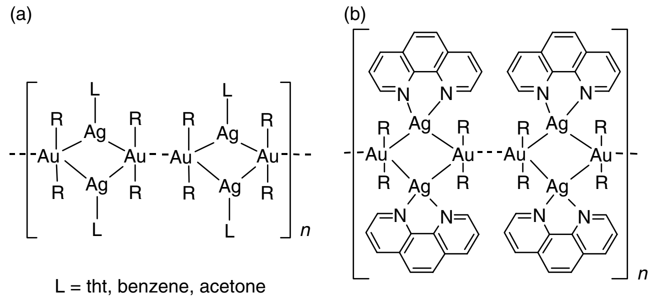


**Figure 2.** (a) Structure of $[Au_2Ag_2(C_6F_5)_4L_2]_n$ complexes, where L = tetrahydrothiophene (tht), benzene and acetone, adapted from Refs 43, 44 and 46. (b) Proposed structure for $[Au_2Ag_2(C_6F_5)_4(phen)_2]_n$ (**1**).

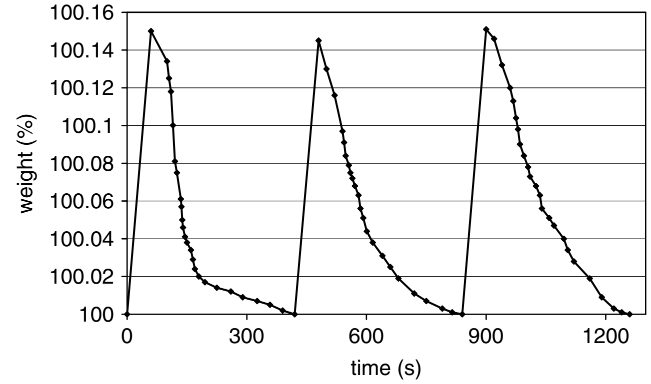
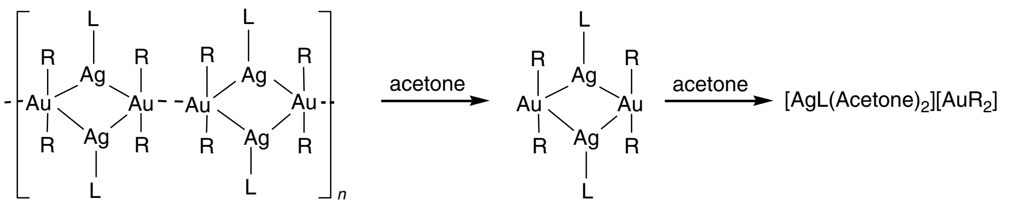


**Figure 3.** Different cycles of mass modification of complex **1** when exposed to acetone vapour for 1 min and without acetone.



**Scheme 2.**

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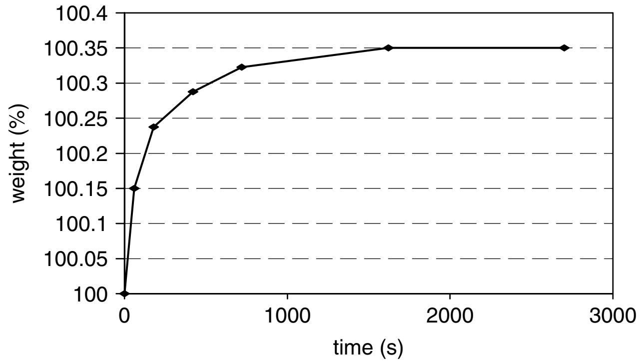

**Figure 4.** Mass gain of complex **1** on exposure to acetone vapour for different times.

desorptions repeatedly; the error of these measurements is 0.045 and the standard deviation is 0.044. The amount of vapour retained increases with time until a maximum is reached at ~30 min (Fig. 4). The important point is that the process is totally reversible.

The total colour change, from yellow to colourless solution, needs quite a big quantity of acetone but small quantities of solvent in the vapour phase are able to produce changes in the yellow colour. The colour change of $[Au_2Ag_2(C_6F_5)_4(phen)_2]_n$ is not spectacular but is enough to be detected by the human eye. Optical fibre sensors are very sensitive and they are able to detect small changes in the reflected optical power (Fig. 1) produced by exposing the chemical complex to VOC vapours.

Figure 5 shows the reflected optical power versus time for five different concentrations of acetone vapour at the wavelength of the optical source (1550 nm). The curves show the response of the VOCs when 0.1, 0.4, 0.7, 0.9 and 1 ml of acetone liquid are placed inside the chamber (200 ml). One can observe that the reflected power decreases when the concentration of acetone increases, the maximum reflected power change being 4 dB. The behaviour observed at the wavelength of 1310 nm is similar, with a maximum reflected power change of 3 dB. In Fig. 5 it is also possible to observe that when the container is opened, at different times in each experiment, the acetone vapour quickly vanishes and the reflected optical power eventually achieves its initial values, first with a deep slope and then more gradually. Although we also tested the laser at 635 nm, it does not give us good results with the complex $[Au_2Ag_2(C_6F_5)_4(phen)_2]_n$.

The sensor used in this work is able to detect acetone even when this organic compound is dissolved in water. This behaviour has been studied with the sensor submerged in 20 ml of water containing 3, 5 or 10 ml of acetone. When the liquid is in contact with the detector one can observe again that the reflected power decreases when the concentration increases, although in these case the responses are lower than with the vapour. Figure 6 shows the response of the sensor at a laser source of wavelength 1310 nm, with a maximum reflected power change of 1.2 dB. When the detector is removed from the water solution at different times in each experiment, the reflected optical power eventually reaches its initial values in a very slow way, perhaps because in these cases the detector must lose the solvent to become dry. Results obtained with the source at wavelength 1550 nm are very similar.

## CONCLUSION

We report here a safe synthesis of $[Au_2Ag_2(C_6F_5)_4(L)_2]_n$ derivatives using $Ag(SO_3CF_3)$ or $[Ag(SO_3CF_3)(tht)]$ instead of the potential explosive $Ag(ClO_4)$. It is important to state that the optical VOC sensor based on the vapochromic material

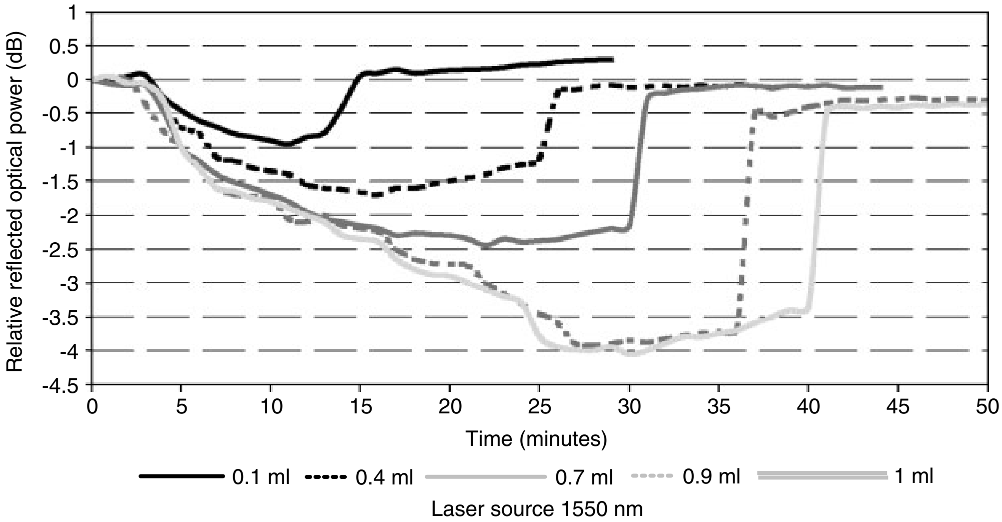

**Figure 5.** Optical fibre VOC behaviour vs. time at different concentrations of acetone vapours with the laser source at 1550 nm.

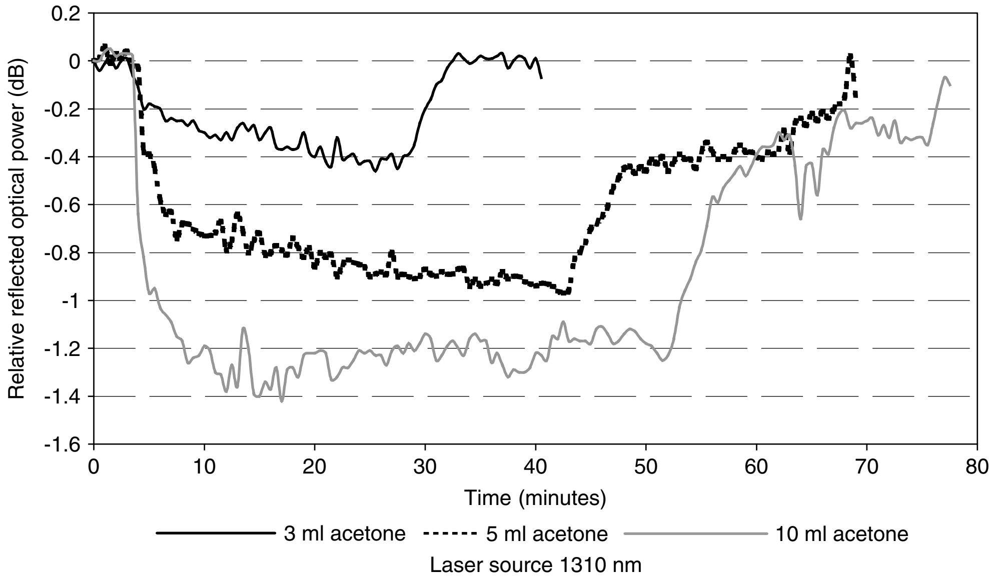

**Figure 6.** Optical fibre VOC behaviour vs. time at different acetone–water solutions with the laser source at 1310 nm.

$[Au_2Ag_2(C_6F_5)_4(phen)_2]_n$ deposited on the end of a standard communication optical fibre is able to detect VOCs not only in the gas phase but also in water solution. Also, due to the reduced dimensions of the sensor, 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 this sensor suitable for use in the petrochemical and chemical industries. Research into other vapochromic materials, including different $[Au_2Ag_2(C_6F_5)_4L_2]_n$, is under way.

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