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Tetrahedron 60 (2004) 8257–8263
Tetrahedron

1,3,5-Triaryl-2-penten-1,5-dione anchored to insoluble supports as heterogeneous chromogenic chemosensor

Mercedes Alvaro, Carmela Aprile, Avelino Corma,* Vicente Fornes, Hermenegildo Garcia* and Encarna Peris

Departamento de Quimica, Instituto de Tecnologia Quimica CSIC-UPV, Universidad Politecnica de Valencia, 46022 Valencia, Spain

Received 5 February 2004; revised 4 June 2004; accepted 16 June 2004

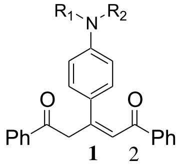
Abstract—*N*-Allyl substituted 1,5-diphenyl-3-(4-*N*-methylaminophenyl)-2-penten-1,5-dione (**1a**) has been immobilized on a polystyrene backbone, on the surface of mercaptopropyl-functionalized silica or inside the cavities of zeolite NaY. These solids either in suspension or in films act as chemosensors of Fe^{3+} and other strong Lewis acid metal ions such as Cu^{2+} and Pb^{2+} in buffered water or ethanol. Brönsted acids in low pH aqueous solutions also produce the response of the sensor. For sensing of Fe^{3+}, depending on the loading of **1a** (typically from 2.5 to 0.5 wt%) the solids can test from 10^{-2} to 10^{-4} M aqueous solutions. The time response can vary from tens of minutes to below a minute depending on hydrophilic/hydrophobic nature of the support and also on the **1a** loading. The solid sensor was reused up to 10 times by regenerating after every use the initial form with NaAcO treatment.

1. Introduction

A strategy to convert a soluble chemosensor into a heterogeneous sensing system could be anchoring covalently an appropriate derivative of the sensor molecule onto an insoluble support.[1,2] Analogous approach is commonly used in heterogeneous catalysis to immobilize active homogeneous catalysts.[3–5] Immobilization of the sensor allows to design systems for automatic continuous sensing. For this purpose organic polymers or inorganic oxides have been frequently used.[6,7] In contrasts, no much attention has been paid to the use of inorganic oxides as supports in spite that they offer the advantage of a large surface area and the possibility to have structured particles with micro- or mesoporosity, while organic polymers have an easy processability.[3,5,8,9]

When anchoring a sensor molecule onto a solid support some new factors, different from homogeneous sensing that require to be properly addressed, may arise influencing the performance of the sensor in solution. Most of differences between solution and surface-anchored sensor may derive from the interaction of the sensor with the solid surface. This interaction could play an unfavourable role reducing the affinity between the sensor and the analyte and leading to a reduced sensitivity of the anchored chemosensor. Also the accessibility of the sensor to the analyte may be reduced when the molecule is immobilized on the internal pores of a porous particle. All these factors may lead to a decrease on the sensitivity, increasing the detection threshold and the response time. These changes are negative in the use of the solids as sensors. On the other hand, reversibility and reusability is another issue of considerable importance for solids sensors that are never considered in solution.

Recently there has been a large interest in the use of 2-penten-1,5-dione derivatives of the type **1** as colorimetric sensors for a series of cations,[10] anions[2] and diacids.[10] Given the insolubility of these molecules in water, most of the analytic tests have been performed in organic solvents such as CH_2Cl_2, or water/organic solvent mixtures what may constitute a limitation of the homogeneous phase sensing methodology.



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a: R_1=CH_3; R_2= CH_2-CH=CH_2

Keywords: Chemosensors; Pyrylium dye; Covalent functionalization.

* Corresponding authors. Tel.: +34963877807; fax: +34963877809 (H.G.).; e-mail: hgarcia@qim.upv.es

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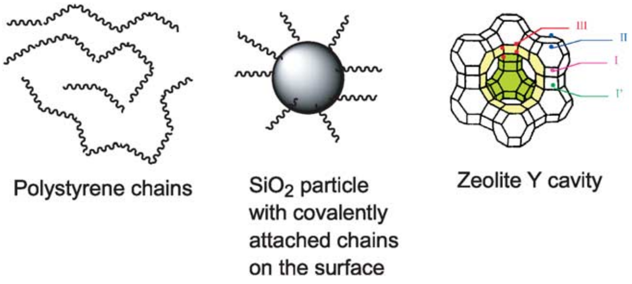
doi:10.1016/j.tet.2004.06.090

Given the generality of these pentendiones **1** as sensors and in order to develop a sensitive device for continuous operation, it would be of interest to support this molecule type on a series of solid supports and determine the ability of the resulting solids to respond as insoluble chemosensors. Herein we describe our results on the covalent anchoring of pentendione derivative, **1a**, on three insoluble supports. We will show our results towards the development of convenient solid chemosensors based on cyclizable pentendione, as well as limitations in response time, sensitivity and reusability and some ways to circumvent or minimize these general problems encountered in heterogeneous sensors.

2. Results and discussion

2.1. Synthesis of the solid chemosensors

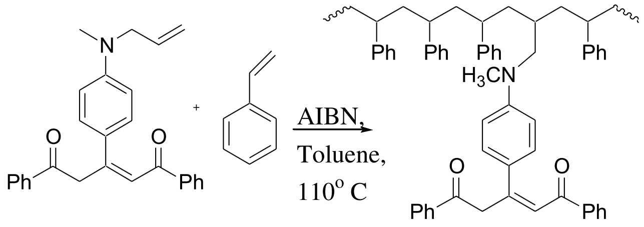
Among the solid supports selected, we tried to cover organic and inorganic supports. One of these supports is a polystyrene backbone to which some pentendione molecules **1a** were introduced during the polymerization step. The advantage of this polymer is that while it is insoluble in water, it can be dissolved in hot toluene so films of this polystyrene-bound sensor (**1a-PS**) can be cast on appropriate substrates. The other two supports are inorganic oxides namely silica and zeolite Y. In the case of the silica the pentendione **1a** can be bonded to the external surface of the amorphous particles (**1a-SiO$_2$**). In contrast NaY zeolite has a crystalline structure containing almost spherical cavities of 13 Å of diameter interconnected tetrahedrally through 12 oxygen ring windows of 7.4 Å in which the pentendione **1a** can be accommodated and immobilized inside the solid (**1a@NaY**). Scheme 1 shows the structure of the zeolite used in this work.



Scheme 1. Pictorial representation of the three supports on which compound **1a** has been immobilized.

To immobilize covalently the sensor to the solids we followed a flexible strategy based on the use of a common pentendione derivative containing an allylic functionality attached to the *N*-atom (**1a**). This compound was obtained by reacting *N*-methyl-*N*-allylaniline with 2,6-diphenylpyrylium ion followed by the opening of the heterocyclic ring. Scheme 2 indicates the reaction sequence followed to prepare the *N*-allyl functionalized pentendione **1a**.

The anchoring of this intermediate on a polystyrene backbone was simply accomplished through AIBN-initiated radical co-polymerization of **1a** and styrene (Scheme 3). The ratio styrene/**1a** was purposely high, so the polymer contains approximately between 0.5 and 2 wt% of chemosensor depending on the **1a** content used in the polymerization. The resulting **1a-PS** polymer is soluble in hot toluene, but insoluble in water and alcohols.

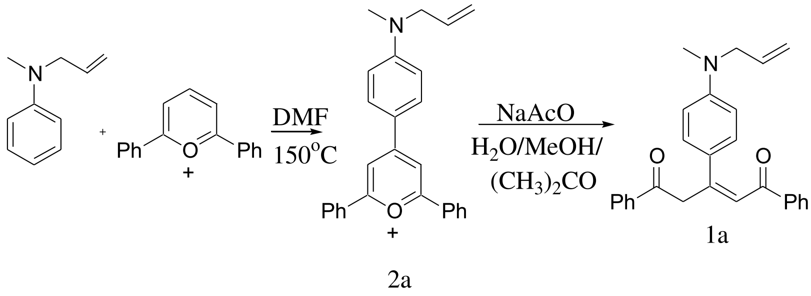


Scheme 3. Co-polymerization of compound **1a** and styrene to form **1a-PS**.

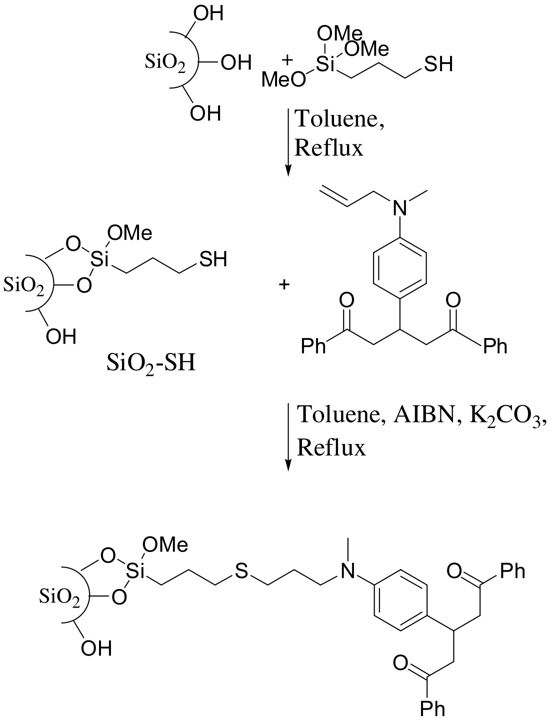
In the case of covalent anchoring of the allyl derivative **1a** on silica we followed a route consisting on the prior modification of the silica by introducing terminal mercapto groups by silylation of the silanol groups. The silica was modified by reaction with 3-mercaptopropyltrimethoxysilane in toluene. Scheme 4 shows the procedure used to anchor the chemosensor **1a** onto the functionalized silica.

Subsequently, modified silica support containing terminal mercapto group (**SiO$_2$-SH**) was reacted with the *N*-allyl-*N*-methyl derivative of pentendione **1a**, which undergoes a radical-chain thiol addition using AIBN as radical initiator as shown in Scheme 4.

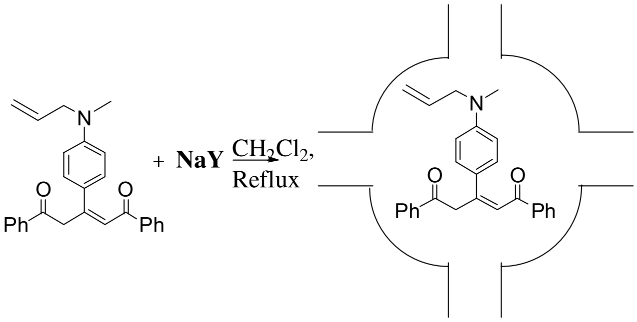
For the solid sensor in which pentendione **1a** is mechanically immobilized (as opposed to covalent anchoring) inside the cavities of porous NaY zeolite (**1a@NaY**), the *N*-allyl group does not play any role but derivative **1a** was also used for sake of synthetic economy. The major factor contributing to support the chemosensor within NaY is the high adsorption capacity of zeolites to include an organic guest in the micropore volume (Scheme 5).



Scheme 2. Synthetic route for the preparation of **1a**.



Scheme 4. Preparation procedure of sensor **1a-SiO$_2$**.

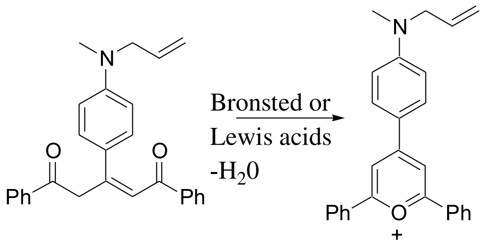


Scheme 5. Adsorption of compound **1a** into the cages of zeolite NaY to form **1a@NaY**.

Encapsulation of 1,3,5-triphenyl-2-penten-1,5-dione, analogous to the substrate **1a** used here, has been successfully achieved by Miranda, Braun et al. through a novel encapsulation strategy.[11] They reported that 2,4,6-triphenylpyrylium ion in water was completely adsorbed in zeolite NaY up to a loading of 25% in weight through the open 1,3,5-triphenyl-2-pentendione. In our case the pentendione **1a** was simply adsorbed into dehydrated NaY zeolite by stirring a suspension of the solid and the organic compound in dichloromethane at reflux temperature.

2.2. Characterization of the solid sensors

All the solids have common spectroscopic features arising from the presence of pentendione **1a**. Optical spectroscopy is particularly relevant since the colorimetric sensing relies on changes in the visible optical spectrum. Depending on whether the sensor can be dissolved (**1a-PS**) or is an insoluble opaque powder (**1a-SiO$_2$** or **1a@NaY**), transmission or diffuse reflectance modes were used to record the optical spectrum. In addition of the interest in optical spectroscopy to characterize spectrophotometrically the visual changes occurring during the sensing, UV/Vis spectroscopy served also to assess the absence or presence of some pyrylium ion **2a** formed spontaneously during manipulation of **1a** in the anchoring procedure according to Eq. (1). This is the reverse of the heterocycle opening shown in Scheme 1.



(1)

In UV spectroscopy the presence of the heterocyclic pyrylium ion can easily be revealed. This characterization

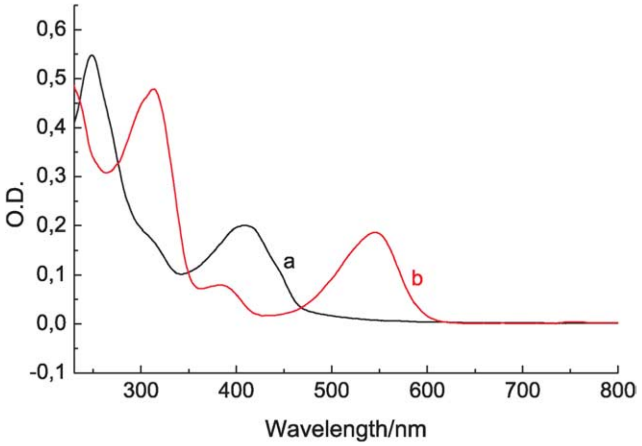


Figure 1. Transmission optical spectrum of pentendione **1a** (spectrum a) and pyrylium ion **2a** (spectrum b) recorded for 10^{-4} M solution in dichloromethane.

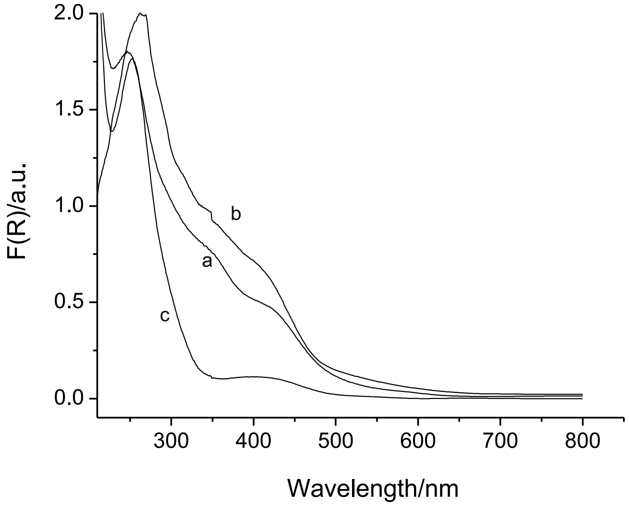


Figure 2. Diffuse reflectance UV/Vis spectra (plotted as the Kubelka–Munk function of the reflectance, F(R)) of **1a** covalently bonded to silica (spectrum a) and polystyrene (spectrum b) or absorbed on NaY (spectrum c).

of **2a** is based on the presence, or absence, of a specific peak, at $\lambda_{max} = 560$ nm, that is responsible for the intense red color of the closed heterocyclic cation **2a**. This band is absent in the pentendione **1a**, that presents a yellow color and has characteristic absorption band at 410 nm. Figure 1 shows the UV/Vis spectra of the pentendione **1a** and pyrylium **2a** ion recorded in dichloromethane solution, while Figure 2 shows some spectra recorded for the solids containing pentendione **1a**.

Figure 2 establishes the absence of the band at 560 nm, indicating that the immobilization procedure has not produced the cyclization of the pentendione **1a**. This is also in agreement with the visual yellow color of all the supports after the immobilization procedure. The presence or absence of this band due to pyrylium ion **2a** will become more relevant later when discussing the chemosensing properties of these solids and the possibility of successful regeneration upon reuse. In some cases, for inorganic supports SiO_2 and NaY, we observed an extensive cyclization during the anchoring or the adsorption procedure as evidenced by the red color of the substrate and by the appearance of the pyrylium band in the visible region. According to Eq. (1) we believe that pyrylium **2a** arises from the acid catalysed cyclization of **1a** during the adsorption. To avoid or minimize the presence of acid sites on the inorganic supports, these solids were neutralized by contacting them with basic solutions.

IR spectroscopy is also a very convenient technique to distinguish between the pentendione **1a** and the pyrylium ion **2a**. While the former shows three bands at 1676, and 1642 cm^{-1} corresponding to the vibration of the carbonyl groups and the C=C double bond present in the dione, the most remarkable spectral feature of the pyrylium ion **2a** is the absence of these bands and the presence of a very intense peak at 1588 and 1573 cm^{-1} corresponding to the stretching mode of the $C=O^+$ bond present in the pyrylium ring. Figure 3 shows the IR of the two compounds.

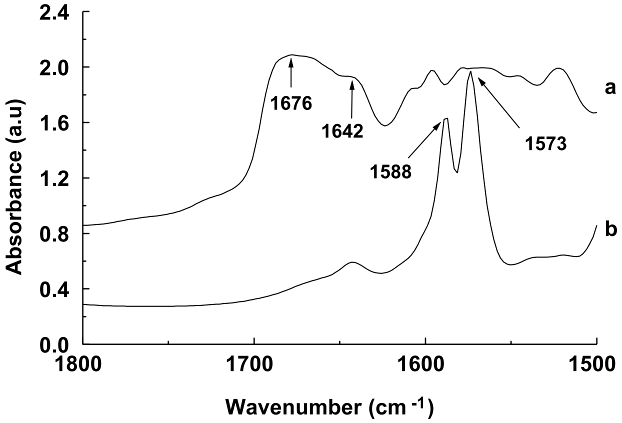


Figure 3. Carbonyl and aromatic region of the FT-IR spectra of compounds **1a** (a) and **2a** (b) recorded at room temperature on silicon wafers.

Previously we have reported[12] that the parent 2,4,6-triphenylpyrylium ion has an intense $C=O^+$ band at 1620 cm^{-1} and the large shift (about 30 cm^{-1}) observed for the *N*,*N*-dialkyl derivative **2a** can be attributed to the electron donor effect of the nitrogen atom being conjugated with the electron deficient pyrylium ring. In the case of the solid sensors the predominant absorption bands are obviously due to the polymeric or to the inorganic supports, but sufficient expansion of the carbonyl and aromatic region allows to detect weak broad bands that are attributable to the low amounts of the pentendione **1a** anchored to the support.

2.3. Use of solid sensors

As aspected in view of the behaviour of pentendione **1a** reported in solution,[1,2] all the solids change the color from yellow to red upon contacting with 10^{-2} M aqueous solutions of $Fe(NO_3)_3$, $Cu(NO_3)_2$ or $Pb(NO_3)_2$. In contrast, aqueous solutions of Al^{3+}, Mg^{2+} and Ca^{2+} or anions (Br^-, HPO_4^{2-}) did not give a positive test at this concentration. In accordance to Eq. (1), it is expected that the heterogeneous sensor systems based on the interconversion of **1a** to **2a** would respond to any Lewis acid cations with sufficient strength to provoke the cyclization of the pentendione through coordination with the N atom in the *para* position of the 4-aryl ring. In principle this cyclization can also be carried out by Bronsted acids and in fact aqueous solutions of HNO_3 (pH = 1) are also able to produce the response of the solid sensors. For this reason, most of the experiments in aqueous media were carried out in buffered solution at pH = 5 using HEPES. At this pH a blank control showed that cyclization of **1a** to **2a** does not occur for reasonable long periods of time.

Besides experiments in suspension performed stirring a solution of Lewis acid cations and the solid sensor, an alternative way of performing the tests was to place the solids as thin films on an inert substrate. For this set-up we covered a glass slide with a thin layer of each of the three water-insoluble solid sensors and assays were carried out by simply dropping a few microliters of the solutions of different cations on the sensor-covered glass.

Upon addition of aqueous solution of Fe^{3+} (pH = 5) the change in the color was progressive in time. In the case of silica and zeolite Y at the lowest loading of **1a** employed (5 mg per g of support) the red coloration was evident in a few minutes and became complete after 30 min. According

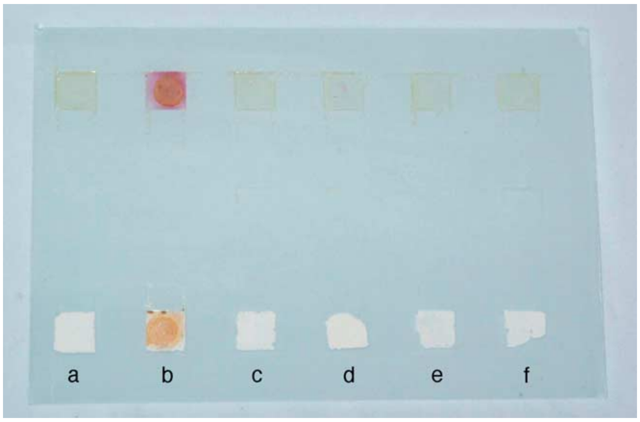


Figure 4. Photograph of a glass plate in which films of **1a-PS** (upper row) and **1a@NaY** (lower row) have been placed as squares. The image was recorded 1 h after dropping 50 μl of distilled water (a) or 10^{-2} M aqueous solution of: Fe^{3+} (b); Mg^{2+} (c); Al^{3+} (d); Br^- (e); HPO_4^- (f).

to the more hydrophobic nature of polystyrene backbone, when pentadione **1a** was covalently anchored on polystyrene the response of **1a-PS** was even significantly slower, the red color developing over 1 h and becoming complete in 5–6 h. Figure 4 shows a photograph of the sensing experiments in which the differences between positive or negative responses can be seen for some analytes.

In fact one of the major problems of the solid supports is the contact time required to observe the response. Obviously, in contrast to the solids sensors, for solution experiments the change in the color is almost instantaneous. As commented above this contact time depends on the hydrophilicity/hydrophobicity of the support. In this regard, the response time of **1a-PS** is dramatically reduced from hours up to less than 1 min when $Fe(NO_3)_3$ is dissolved in ethanol instead of water. Notably for these ethanolic solutions the response of **1a@NaY** requires longer time than for **1a-PS**. We also observed that the response time becomes shorter when solids sensors with more than 0.5 wt% contents of **1a** are used. Also the intensity of the color increase with loading of **1a**. Thus, by controlling the loading of **1a** on the solid one can on one hand shorten the response time and on the other to decrease the detection threshold of the film. The problem of using solids with high **1a** loading is the reusability as it will be commented above.

It was of interest to determine by optical spectroscopy whether or not the change in the color is accompanied by a partial chemical conversion between the pentendione and the pyrylium form as indicated in Eq. (1) in agreement with the chemosensing operation of the sensing system. We took the absorption bands at 440 and 550 nm as specific of the open form **1a** and heterocyclic form **2a** of the sensor system, respectively. We found that the red color, characteristic of the visual positive test as shown in Figure 4, corresponds to a true chemical change from **1a** to **2a**. Figure 5 shows a UV/Vis spectrum 30 min after addition of 10^{-2} M solution of $Fe(NO_3)_3$ in which the band at 550 nm is observed. This support the chemical interconversion between the open and the cyclic form.

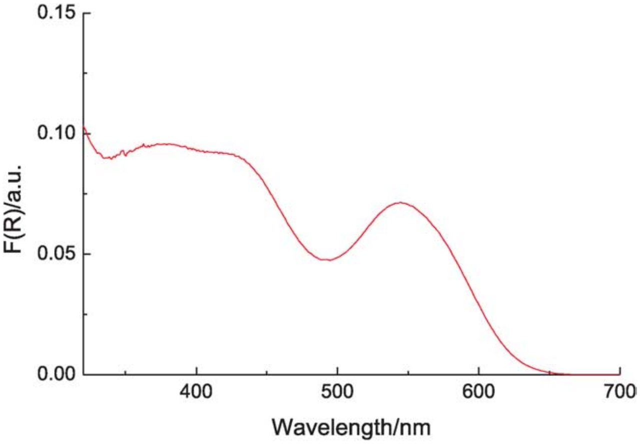


Figure 5. Diffuse reflectance UV/Vis spectrum of a **1a@NaY** solid 30 min after contacting with 1 ml of a 10^{-2} M aqueous solution of $Fe(NO_3)_3$. The visual appearance of the solid is red. For the initial diffuse reflectance spectrum of the sample see Figure 1.

The response of the glass coated sensors at 0.5 wt% loading of **1a** was also visually observable for 10^{-3} M concentration of Fe^{3+}, while for more diluted solutions not relevant response was observed.

As commented above, the detection threshold can be lowered, the visual response reaching 10^{-4} M when the concentration of **1a** is increased to 25 mg per gram of support. This loading also gives much faster response than lower contents of **1a**. However, high contents of **1a** give problems in terms of reusability.

2.4. Reuse of the solid sensors

In fact when working on solid chemosensors, one point of critical importance is the possibility of reuse by regeneration of the initial sensor form after the testing. In the case considered here and according to Scheme 2, it should be possible to reopen the heterocyclic pyrylium ion **2a** to pentendione **1a** by treatment with an aqueous base solution. As expected, upon addition of some drops of 10^{-1} M NaOAc onto the film of sensor the red color gradually turned into the yellow and the optical spectrum changed from the one corresponding to pyrylium to that of the pentendione. Figure 6 shows the spectra corresponding to three consecutive 10^{-2} M $Fe(NO_3)_3/10^{-1}$ NaOAc cycles using **1a@NaY** as heterogeneous sensor.

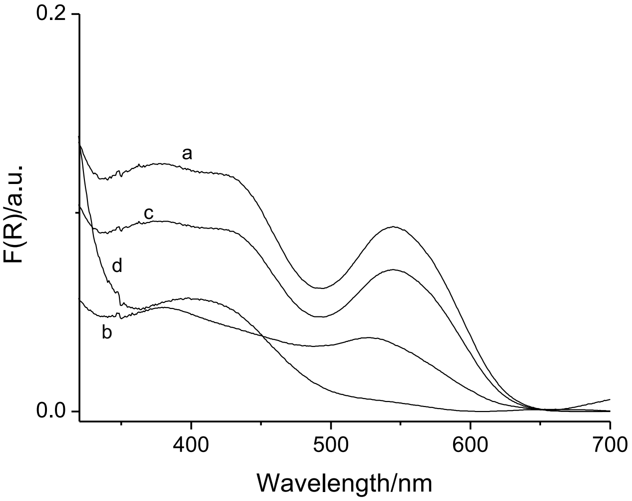


Figure 6. Diffuse reflectance UV/Vis spectra of the same sample of **1a@NaY** (loading 0.5 wt%) submitted, respectively, to the following treatments: (a) 10^{-2} M Fe^{3+}, 30 min; (b) 10^{-1} M NaAcO, 30 min; (c) 10^{-2} M Fe^{3+}, 30 min; (d) 10^{-1} M NaAcO, 30 min.

As it can be seen in this figure, UV/Vis spectroscopy reveals that the **1a@NaY** system undergoes a certain fatigue and the reversibility of the conversion between the open and the closed form is not complete after a few cycles as evidenced by the incomplete disappearance of the 560 nm band characteristic of **2a**. The higher the loading of **1a**, the lesser the reversibility of the system. It is worth commenting that **1a@NaY** is in fact the less reversible of the three insoluble solid sensors films since it is expected that Fe^{3+} will gradually exchange the Na^+ of the zeolite upon extensive reuse. In this regard **1a-SiO$_2$** or **1a-PS** are more reusable

Figure 7. Photograph of two dichloromethane solutions (3 ml) of **1a**-**PS** (50 mg in the first run) that has to be submitted to 10 consecutive test-recovery cycles. Left: upon addition of 500 μl of an 2.5×10^{-3} M ethanolic solution of $Mg(OAc)_2$. Right: after addition of 50 μl of an 2.5×10^{-3} M solution of $Fe(NO_3)_3$.

systems. For these two solids at 0.5 wt% loading the recycling of the sensor and the regeneration was performed at least 10 times without remarkable differences in the visual behaviour of the chemosensor. Figure 7 shows a photograph of a negative 2.5×10^{-3} M ethanolic solution of $Mg(OAc)_2$ and a positive 2.5×10^{-3} M ethanolic solution of $Fe(NO_3)_3$ test using **1a**-**PS** after 10 consecutive reuses regenerating every time the pentendione form by treatment with 10^{-2} NaOAc aqueous solution.

3. Conclusions

Covalently binding or adsorption of pentendione **1a** to several inorganic and organic supports is a viable strategy to transform this compound soluble in organic solvent into an insoluble solid sensor for Fe^{3+} and other strong Lewis acids and cations. In aqueous solution, the recoverable sensors also respond to Brönsted acids.

The three major problems are the increase in the response time, the lesser sensitivity and the reusability of the solids. The time of response and sensitivity are clearly modulated by the hydrophilicity of the support and the loading of the dye. Solid sensors containing 2.5 wt% of compound **1a** may show the response time below minutes and can detect below 10^{-3} M concentration. Reusability relies on the reversibility of the heterocyclic ring opening under basic conditions to regenerate the open pentendione form. The solid support plays a role in the system by hydrophobic/hydrophilic interaction with the solvent and also by promoting undesirable spontaneous cyclization of pentendione **1a**. Silica and zeolite are more adequate for sensing in water, while polystyrene gives shorter response time in ethanol. We are expanding this strategy to the development of other chromogenic heterogeneous sensors.

4. Experimental

4.1. Synthesis of organic compounds

4.1.1. Synthesis of *N*-allyl-*N*-methylaniline..[13] *N*-Methylaniline (535.5 mg, 5 mmol) was dissolved in dry THF (10 ml) and ^tBuOK (561.4 mg, 5 mmol) was added. The mixture was stirred for 1 h at 0 °C under N_2 atmosphere and allyl bromide (604.9 mg, 5 mmol) was added. The suspension was warmed at room temperature and magnetically stirred for 24 h. Then, the reaction was washed with a 1 M solution of HCl and extracted with CH_2Cl_2. The organic layer was washed with NaOH, dried with Na_2SO_4 and evaporated under vacuum. The compound (35%) was obtained as yellow oil after chromatography using a mixture of hexane/diethyl ether (10/1) as eluent. ^1H NMR ($CDCl_3$) δ: 2.98 (s, 3H, CH_3), 3.94 (d, $J=4.8$ Hz, 2H, CH_2N), 5.14–5.22 (m, 2H, $CHCH_2$), 5.77–5.90 (m, 1H, $CHCH_2$), 7.22–7.28 (5H, ArH). ^{13}C NMR ($CDCl_3$) δ: 36.6, 55.9, 113.0, 116.7, 117.0, 129.7, 134.4, 150.1.

4.1.2. Synthesis of compound 2a. *N*-Allyl-*N*-methylaniline (160.3 mg, 1.1 mmol) was dissolved in DMF (3 ml) and the 2,6-diphenylpyrylium perclorate (724.4 mg, 2.2 mmol), synthetized as described in the literature,[14,15] was added. The mixture was stirred at reflux temperature for 3 h, then cooled at room temperature and stirred for 20 h. The solvent was removed under reduced pressure and the resulting brownish, red oil used for the next step without purification.

4.1.3. Synthesis of compound 1a. Sodium acetate (183.3 mg, 2.23 mmol) was dissolved in a mixture of water (0.6 ml), methanol (1.9 ml) and acetone (3.8 ml). The crude compound **2a** was added, the mixture was stirred for 15 h at room temperature and for 10 h without stirring.

The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography using diethyl ether as eluent yielding pentendione **1a** (55%) as yellow oil.

^1H NMR ($CDCl_3$) δ: 3.01 (s, 3H, CH_3), 3.92 (d, $J=4.5$ Hz, 2H, CH_2N), 4.91 (s, 2H, CH_2COPh), 5.08–5.24 (m, 2H, $CHCH_2$), 5.63–5.96 (m, 1H, $CHCH_2$), 7.14–7.98 (m, 14H, ArH). ^{13}C NMR ($CDCl_3$) δ: 36.6, 55.9, 112.4, 116.8, 126.7, 127.0, 128.1, 128.6, 128.9, 129.2, 129.4, 129.6, 133.5, 135.7. HPLC-MS (electrospray) 396.2 ($M+H^+$). Combustion chemical analysis: Exp (%): C 80.40, H 6.50, N 3.09; calculated for $C_{27}H_{25}NO_2$ (%): C 82.00, H 6.37, N 3.54.

4.2. Preparation of the solid sensors

Compound **1a-PS**. Styrene (1 g) was dissolved in toluene (15 ml), a solution of **1a** (10 mg) in toluene (5 ml) and AIBN in catalytic amount were sequentially added. The mixture was stirred at reflux temperature under N_2 atmosphere for 3 h, then cooled at room temperature. The solvent was removed under reduced pressure yielding **1a-PS** as yellow solid.

Compound **1a@NaY**. The zeolite NaY (Aldrich, 1 g) was dehydrated by calcination at 500 °C for 6 h, then cooled under vacuum and suspended in CH_2Cl_2 (15 ml). A solution of **1a** (10 mg) in CH_2Cl_2 (5 ml) was slowly added and the mixture was stirred at 40 °C for 3 h. The solid **1a@NaY** was obtained as yellow powder after filtration and extensive washings with CH_2Cl_2.

Compound **1a-SiO₂**. Silica (BASF, 4 g) was dried at 300 °C under vacuum for 6 h and suspended in dry toluene (40 ml). 3-Mercaptopropyl trimethoxysilane (4 ml) was slowly added and the mixture was stirred for 48 h at 110 °C. The resultant solid was filtered, dried and washed with CH_2Cl_2 in a Soxhlet apparatus to remove the unreacted silane. The modified SiO_2-SH (1 g) was then suspended in toluene (15 ml) and $NaHCO_3$ (200 mg) was added to neutralize the acidity. The suspension was stirred for 20 min then a solution of **1a** (10 mg) in toluene (5 ml) and AIBN, in catalytic amount were sequentially added. The reaction was stirred at reflux temperature for 24 h, then filtered and washed with $CH_2Cl_2\cdot$ yielding **1a-SiO$_2$** as yellow solid.

4.3. General sensing experiments.

Suspension test. The solid sensors **1a-SiO$_2$** or **1a@NaY** (100 mg) were suspended in an aqueous solution at pH 6.7 (buffered with HEPES). Some drops of the nitrate or sodium salts of the ions (from 10^{-2} to 10^{-4} M in water) Fe^{3+}, Al^{3+}, Mg^{2+}, Br^{-}, HPO_4^{-} were then added to each suspension and then the mixture was magnetically stirred.

Films. **1a-PS 1a-SiO$_2$** and **1a@NaY** was dissolved in hot toluene (1 ml) and some drops of this solution were cast on a glass previously covered with scotch tape to define squares (1 cm^2). Alternatively, **1a-SiO$_2$** or **1a@NaY** were dispersed in acetylacetone/water (1:10) and the paste cast onto the glass slide. After drying the films, few μl of the nitrate or sodium salts (from 10^{-2} to 10^{-4} M in water or ethanol) of the ions Fe^{3+}, Al^{3+}, Mg^{2+}, Br^{-}, HPO_4^{-} were then dropped over the film.

Acknowledgements

Financial support by the Spanish Ministry of Science and Technology (MAT 2003-1226) and Generalidad Valenciana (grupos03-020) is gratefully acknowledged. Carmela Aprile thanks the Fundation Jose Royo for a postdoctoral scholarship.

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