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Review

Chemodosimeters and 3D inorganic functionalised hosts for the fluoro-chromogenic sensing of anions

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Contents

Abstract

We report here recent examples developed in our research group on the development of novel chemodosimeters for fluoro-chromogenic anion sensing. For instance, squaridine, pyrylium and pent-2-en-1,5-dione dye scaffoldings have been used to obtain highly specific chromo-fluorogenic responses for anions such as cyanide, sulfide or certain carboxylates in water or mixed aqueous solutions. We will also report new examples on the use of "smart sensory materials" based on nanoscopic inorganic structures as bio-mimetic hosts for anion sensing. These systems combine molecular ideas and 3D solid pre-organised features as new design concepts for the development of organic/inorganic hybrid materials for recognition/sensing protocols. For instance, the functionalisation of siliceous mesoporous materials with ureas, thioureas, guanidinium groups or saccharides and suitable dyes has resulted in enhanced fluoro-chromogenic sensing of anionic species such as fatty acids, citrate or borate.

Keywords: Anion sensing; Chemodosimeters; Hybrid materials; Supramolecular systems

1. Introduction

In the last years the field of supramolecular chemistry of anions has been growing in interest [1]. Especially a large amount of work has been devoted to the synthesis of sophisticated and selective receptors. The presence of binding site is a common feature in the design of anion receptors. These binding sites are composed by different coordination subunits arranged in certain topologies in order to achieve high degree of complementarity with the target anion [2–7]. The distinction between receptor and chemosensor is very subtle and relies in the presence of an additional unit (called "signalling subunit") capable of given reliable information about the binding event [8]. Electrochemical shifts of the redox potentials in redox-active molecules [9–13], fluorescence [14–17] and colour changes [18–20] have been the most popular output signals in the development of chemical sensors. The inherent facility in which a fluorescence or UV–vis spectra are recorded and the fact that change upon anion coordination could be observed to the naked-eye have induced a clear preference of researchers towards the development of optical sensors for anions [18]. A great variety of fluorescent compounds (polycyclic aromatic hydrocarbons and

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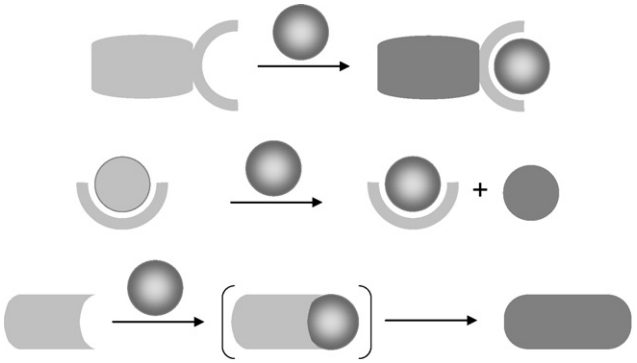


Fig. 1. Schematic representation of the three approaches employed in the development of optical sensors for anions. From top to down: binding site-signalling subunit approach, displacement assays and the chemodosimeter approach.

organic heterocycles) and organic dyes (also generally heterocyclic compounds) are used as signalling subunits.

Three main approaches have been used in the development of optical sensors for anions (see Fig. 1). These differ in the manner in which the binding site or reactive site and the signalling subunit are arranged. In the "binding site-signalling subunit" approach the two parts are linked through a covalent bond [21]. The interaction of the target anion with the binding site induced changes in the electronic properties of the signalling subunit resulting in a sensing of the target anion. The displacement approach is based in the formation of binding site-signalling subunit "molecular ensembles", where the coordination of a certain anion with the binding site results in the release of the signalling subunit into the solution with a concomitant change in their optical characteristics [20]. A third approach to the determination of anions via chromo-fluorogenic protocols is the so called "chemodosimeter approach" that takes advantage of usually specific anion-induced reactions coupled with selective changes in fluorescence or in colour [22]. A great variety of optical sensors for anions has been synthesised by using one of the three approaches cited above [18].

We show here some of our recent contributions to the field of anion sensing via the use of chromo-fluorogenic protocols. In the first part we will detail the use of several chemodosimeters for the selective sensing of certain anionic species. This is an attractive approach that usually shows a high degree of selectivity and large spectroscopic shifts. In the second part of this paper we show new approaches to anion sensing based on the use of nanoscopic inorganic materials as a suitable way to enhance selectivity and applicability.

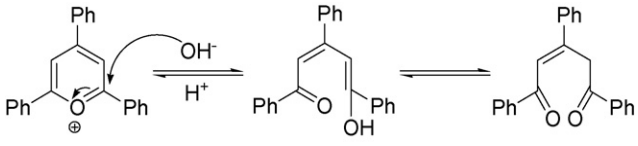
2. Chemodosimeters for anion detection

Among the three approaches mentioned above for anion determination using fluorogenic or chromogenic protocols, probably the less currently used is the chemodosimeter approach. However, in recent years, papers published dealing with this topic have increased continuously [23,24]. These chemodosimeters take advantage of specific anion-induced reactions. They are generally irreversible reactions resulting in a significant chemical transformation involving the rupture and formation of several covalent bonds. Additionally, they are usually coupled to very remarkable spectroscopic modulations. The use of this approach shows some advantages, when compared with the other two protocols, as the high selectivity reached and also a cumulative effect that is related with the anion concentration. Some of the efforts we have carried out in relation to the synthesis of optical systems for anion determination have focused on the use of specific anion-induced chemical processes using organic dyes such as pyrylium derivatives, squaridines anthraquinones and subphthalocyanine aromatic rings.

2.1. Using pyrylium derivatives

Benzene and pyrylium moieties present some structural similarities due to the presence of a delocalized π-cloud in six-atom planar rings. The only difference between both groups is the substitution of one carbon atom by one oxygen atom leading to the corresponding structure bearing a positive charge in the pyrylium [25]. The presence of this positive charge induced an important perturbation of the π-cloud that is reflected in the appearance of partial positive charges at the carbon atoms in the 2-, 4- and 6-positions. This accounts for the fact that pyrylium salts are much more reactive towards nucleophiles than the corresponding benzene or pyridinium salts, as might be expected because of the higher electronegativity of oxygen when compared with carbon and nitrogen. The presence of alkyl or aryl groups at the 2-, 4- and 6-sites help to moderate this reactivity and many of the known pyrylium derivatives have substituents at these sites. One derivative (2,4,6-triphenylpyrylium tetrafluoroborate) has been extensively used as photosensitizer in a wide range of photochemical reactions and processes [26].

One of the most characteristic properties of the pyrylium ring is nucleophilic addition. This attack results in the opening of the pyrylium ring giving a pent-2-en-1,5-dione moiety that is in equilibrium with the corresponding enol tautomer (see Scheme 1). When the nucleophile is an hydroxide anion the opening of the pyrylium ring is fully reversible and, upon addition of protons, the pent-2-en-1,5-dione moiety suffer cyclization and generates again the pyrylium ring (see Scheme 1). Primary amines, thiols, cyanide and hydroxide have also been reported to act as nucleophiles and also induce ring opening [25]. Additionally, the pyrylium group is a strong electron acceptor and its appropriate integration into a molecular scaffolding with a donor group (such as an anilinium ring) yields deeply coloured dyes. As we will see below, such dyes with charge transfer character and with a reactive pyrylium group, have proven to be suitable candidates for use in sensing protocols via anion-induced ring opening – cyclization routes.



Scheme 1. Transformation of pyrylium ring to the diketone form.

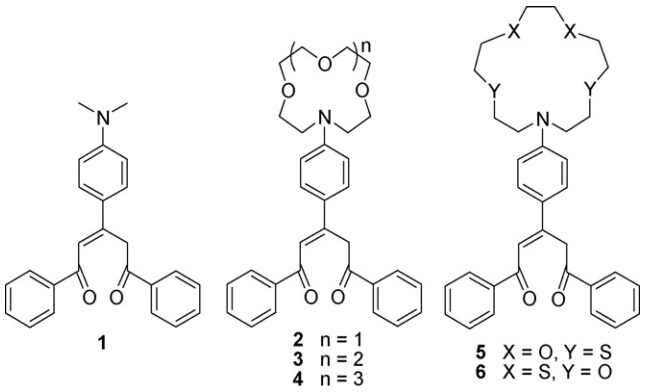


Fig. 2. 1,3,5-Triarylpent-2-en-1,5-diones employed as chemodosimeters for anion sensing.

The 1,3,5-triarylpent-2-en-1,5-diones **1**–**6** (see Fig. 2) containing an anilinium group and a dienone were synthesized by an aromatic electrophilic substitution reactions between 2,6-diphenylpyrylium perchlorate with different N-substituted anilines [27].

They are yellow, but variations in the pH of dioxane–water 70:30 solutions resulted in dramatic colour changes. Thus, **1**–**6** at basic pH show a band centred at 400 nm, but turned magenta at acidic pH due to the appearance of a new band at ca. 550 nm assigned to the formation of the highly delocalized pyrylium ring (see Fig. 3). The pH range in which the pentendione-to-pyrylium transformation takes place is in the range 2–5 for all the six receptors. In this pH range protonation of the aniline nitrogen atom is also expected to take place.

The remarkable property these compounds possess, which allow them to be used as chromogenic anion chemosensors, is that the pH at which the cyclization process occurs can be modulated by the presence of certain anions [27]. This can, for instance, be observed in Fig. 4 which plots the absorbance observed at 550 nm at different pH values for a mixture of compound **5** and various anions (chloride, bromide, phosphate,

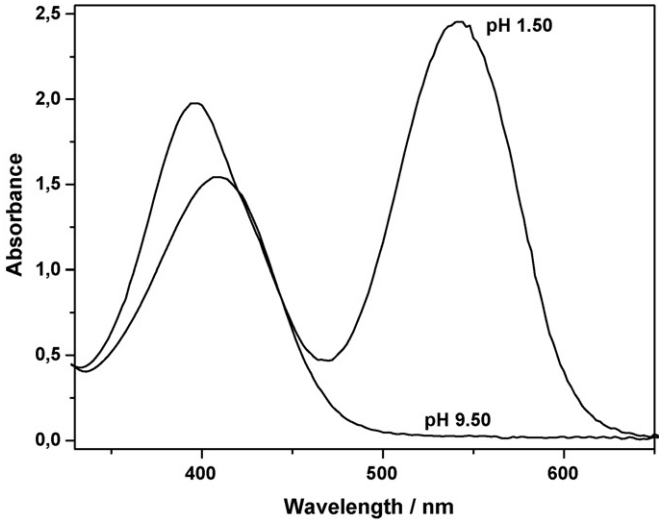


Fig. 3. UV–vis spectra of chemodosimeter **1** at acidic and basic pH in dioxane–water 70:30 mixtures.

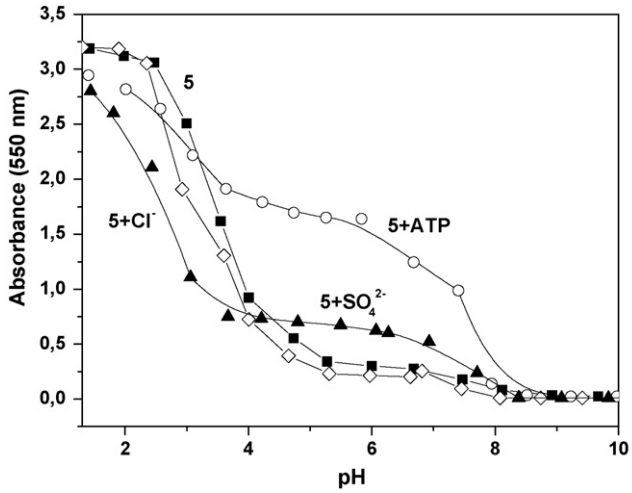
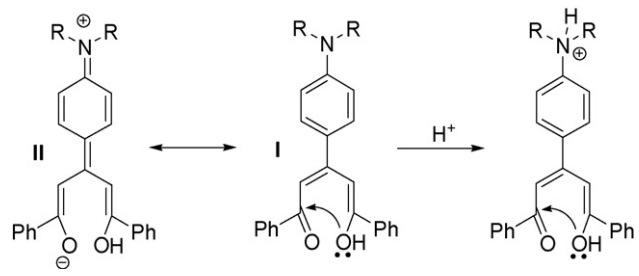


Fig. 4. Absorbance at 550 nm for chemodosimeter **5** in the presence of equimolar quantities of selected anions in dioxane–water 70:30 mixtures and at different pH.

sulfate, GMP, ADP or ATP). As can clearly be seen most anions do not induce significant shifts of the pH at which the cyclization of **5** takes place, except for ATP which is the only anion capable of inducing a remarkable diketone-to-pyrylium transformation at neutral pH (6.5–7.5). This graphic indicates that yellow solutions of **5** at pH 6 are selectively transformed to red in the presence of ATP, pale red in the presence of sulfate, whereas they remain yellow in the presence of bromide, chloride, phosphate, GMP or ADP. For the remaining receptors **1**–**4** and **6** the response is less selective and colour modulation from yellow to magenta at neutral pH was observed in the presence of the anions sulfate, ADP and ATP. This yellow-magenta colour shift for **5** detected upon addition of ATP is not only selective and easy to detect to the naked-eye, but also quite sensitive allowing a detection limit of about 40 ppm of ATP using standard spectroscopic techniques.

To explain the anion-induced cyclization of the 1,5-dienones, cyclization must result from nucleophilic attack of the hydroxyl group of the enol tautomer at C1 of the carbonyl group (see structure **I** in Scheme 2). When the amine is not protonated (neutral and basic pH) the electron density at C1 is too high; in other words, the resonance structure **II** makes a significant contribution and, hence, nucleophilic attack is not favoured. Upon protonation, the nitrogen lone pair is engaged, and structure **II** does not play any role. As a consequence, one would expect



Scheme 2. Proposed resonance structures involved in the ring closure of 1,5-pentanediones to the corresponding pyrylium cations.

C1 to be more electrophilic and thus subject to attack by the enol. To explain the colour change observed in the presence of certain anions, consider that structure **I** contains functional groups such as amine, enol and carbonyl that are capable of coordinating anions through electrostatic forces or hydrogen bonding. By such coordination it could be possible to modulate the nucleophilic character of the hydroxyl oxygen atom of the enol tautomer or the electrophilic character of the C1 carbonyl carbon atom.

The cyclization from dienone to pyrylium was also used for the discrimination of isomeric carboxylates in mixed aqueous environments [28]. This was based on the idea that certain carboxylates, such as ATP, might interact via hydrogen bonding with the 1,5-dienone framework. The sensing studies were carried out using a dioxane/water (70:30, v/v) solutions of **1** at pH 6. At this pH the solution of **1** remains yellow in the presence of the mono-carboxylates acetate and benzoate and in the presence of dicarboxylates such as terephthalate and $^{-}OOC\text{-}(CH_2)_n\text{-}COO^{-}$ (succinate $n=2$, glutarate $n=3$, adipate $n=4$, pimelate $n=5$ and suberate $n=6$). In contrast a colour modulation to magenta was observed in the presence of oxalate and malonate (Fig. 5). This remarkable colour change is, as stated above, a result of the anion-induced selective cyclization of **1** to give the coloured 2,4,6-triphenylpyrylium cation. Also an isomeric colorimetric discrimination between maleate and fumarate was found. Thus, solutions of **1** remained yellow in the presence of the *trans* isomer (fumarate), but changes colour to magenta in the presence of the *cis* isomer (maleate) (see again Fig. 5).

All these dicarboxylate discriminations were also observed when using the 1,5-dienones **2**–**6**, strongly suggesting that the interaction of the anions with the receptors involves a fragment that is common to all of them; the pent-2-en-1,5-dione group. Thus, although diones cannot bind to carboxylates, the corresponding enol tautomers can form hydrogen bonds with the anions (see the upper part of Scheme 3). From all the dicarboxylates studied, only oxalate, malonate and maleate ions gave colour modulations. A closer look to the structures of these dicarboxylates show that these three anions have in common as special feature the presence of two carboxylate groups in close proximity. We believed that ability of these guests to bind the hydroxyl group of the receptor via both carboxylate groups would result in the formation of stronger hydrogen bonds and, therefore, in an enhancement of the nucleophilic character of the hydroxylic oxygen atom. We referred to this action as "tweezer-like" behaviour, bearing in mind that only "tweezer" shaped diacids are able to act as chelating ligands towards the OH group, whereas other diacids or monoacids do not. Scheme 3 tentatively describes the steps in the shape-induced recognition process; the tweezer-like carboxylate groups serve to disrupt the hydrogen atom from the hydroxyl oxygen atom, which induces nucleophilic attack at the C1 carbon, with subsequent cyclization occurring to give the magenta pyrylium cation. Colorimetric recognition of the tweezer-like dicarboxylates appears to be of general application as the yellow receptor **1** also changes colour to magenta in the presence of phthalate anions, whereas they remain yellow in the presence of isophthalate or terephthalate.

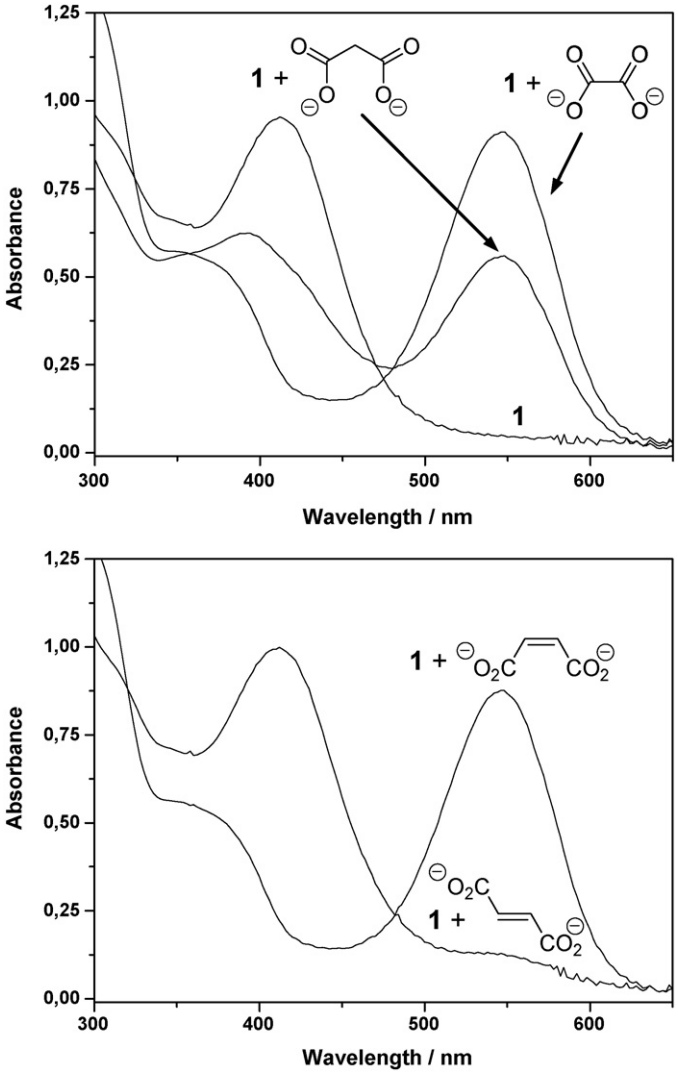
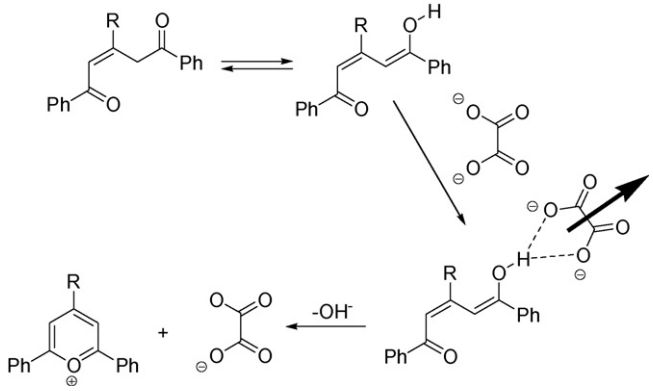


Fig. 5. Visible spectra of **1** at pH 6 (buffered with HEPES 0.01 M in dioxane–water 70:30 (v/v) in the presence of oxalate, malonate (on the top), maleate and fumarate (on the bottom).



Scheme 3. Proposed mechanism of cyclization by nucleophilic attack of the oxygen atom to the C1 carbon. The Scheme also shows the proposed formation of hydrogen bonds between the dianion and the hydroxyl group.

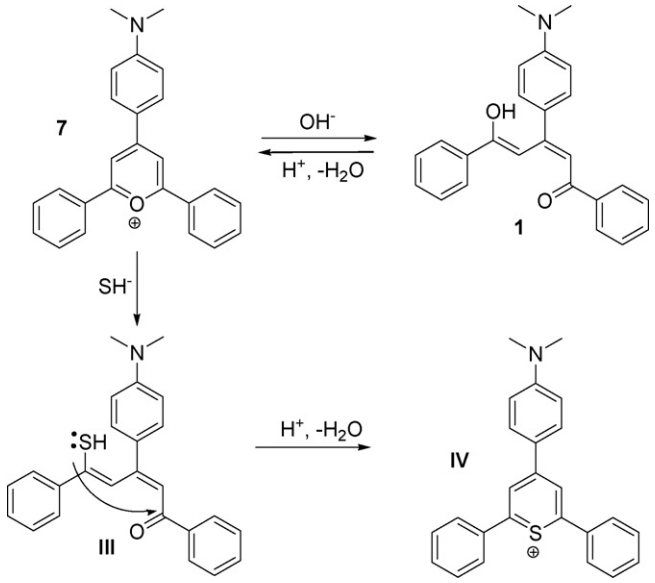
As it is indicated in Scheme 3 the anion is acting as catalyst for the cyclization. This was also confirmed with the determination of the rate constants for the cyclization process that was found to be 149.3, 62.6 and 148.7 M^{-1} s^{-1} for oxalate, malonate and maleate. Molecular modelling calculations of the interaction of the enol tautomer of **1** with different anions were also in agreement with the mechanism outlined in Scheme 3. Thus we found that the strength of the hydrogen bond interaction between the carboxylate and the hydroxyl group of the enol tautomer depends on the nature of the anion and that oxalate, malonate and maleate anion tend to form stronger hydrogen bonds than other carboxylates enhancing the electron density of the oxygen atom of the hydroxyl group and therefore its nucleophilic character. The recognition processes observed with the tweezer-like dicarboxylates match with supramolecular ideas that guests (in our case anions) do not only have charge or size, but also a certain shape (in this case, proximity between carboxylate groups). As far as we know, this is one of the very few examples reported for isomeric discrimination using colorimetric reagents and still today there are few reports dealing with the use of synthetically constructed receptors for the colorimetric sensing of carboxylate anions in aqueous environments.

The examples described above related with the chromogenic sensing of ATP and tweezer-like carboxylates are based on the interaction of the anions with the pent-2-en-1,5-dione framework. Additional to these studies we have also found selective recognition of certain anions (sulfide and cyanide) based on the nucleophilic addition of these anions to the pyrylium ring.

Sulfide is an inorganic anion used by humans in a large number of applications and also can be generated from microbial reduction of sulfate by anaerobic bacterium or formed from the sulfur-containing amino acids in meat proteins [29]. As a consequence of this, the sulfide anion might be found in water giving the well known and disagreeable "rotten eggs" smell. The design of new and improved methods for detection and sensing of sulfide anion can be of interest mainly because the high toxicity of the anion sulfide in human body. Thus, for instance, it has been reported to irritate mucous membranes and can even cause unconsciousness and respiratory paralysis [29].

The design of a chromogenic chemosensor for sulfide anion was based on the use of 2,4,6-triphenylpyrylium derivatives and on the well-known reactivity of the pyrylium cycle [30]. Thus it is well-known that pyrylium salts can be easily transformed into the parent thiopyrilium derivatives as shown in Scheme 4. Nevertheless, the conversion from pyrylium to thiopyrilium has never attracted attention as a potential colorimetric reaction. This has been so, because most of the triarylpyrylium derivatives are yellow as usually also are the analogous thiopyrylium. However, the use of a similar reactive motif coupled with the use of 2,4,6-triaryl-pyrylium cations bearing in the *para* position of the 4-aryl group an amine leads to remarkable colour variations.

The pyrylium–thiopyrylium transformation takes place in two steps as shown in Scheme 4. Thus, as we have seen above, the pyrylium ring can undergo nucleophilic addition to the C1 carbon. For instance, OH^- attack results in the formation of the yellow derivative **1**. In a similar manner, reaction with hydrogen sulfide results in the formation of the yellow compound



Scheme 4. Structure of chemodosimeter **7** and reactivity with OH^- and SH^-.

III. As we have seen above, when acid is added to solutions of **1**, cyclization occurs, and the magenta pyrylium **7** is obtained (λ_{max} = 540 nm; ε ca. 3×10^4 L mol^{-1} cm^{-1}). In contrast the addition of acid to the derivative **III** results in the formation of the thiopyrylium blue cation **IV** (λ_{max} = 580 nm). This transformation occurs even in mixtures containing quite a high percentage of water. Sulfide detection is therefore carried out in two steps, first solutions of **7** in water:acetonitrile (1:1, v/v) are buffered at pH 9 and mixed with 30 equivalents of different anions such as fluoride, chloride, bromide, iodide, acetate, benzoate, sulfide, phosphate, sulfate, nitrate and cyanide. After 2 min, 30 μL of H_2SO_4 (30%) were added to induce cyclization (see Scheme 4). Among the different anions tested only the sulfide anion gave a colour change from magenta to blue, making the reaction and colour change highly specific (see Fig. 6).

Another anion for which we have been developing chromofluorogenic chemosensors is cyanide. This is a very toxic anion

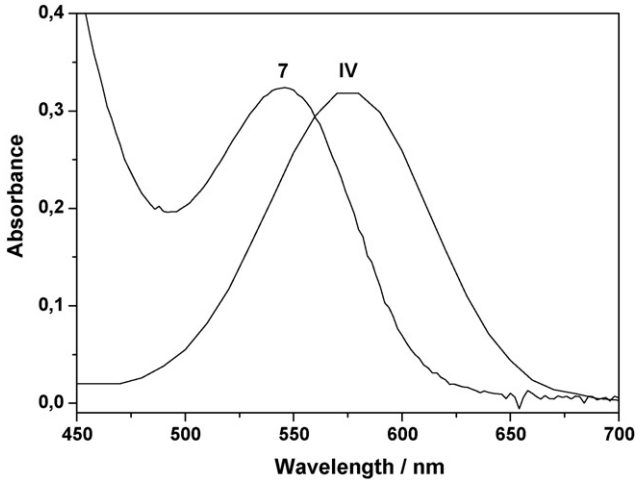


Fig. 6. Visible spectra of chemodosimeter **7** and the thiopyrylium derivative **IV** in acetonitrile–water 50:50 (v/v).

that, despite its sharp toxicity, is still used in a number of applications, i.e. electroplating, mining, metallurgy, etc. Additionally, cyanide can also be present in certain foods such as cassava roots, pits of certain fruits and bitter almonds. The toxicity of cyanide derives from its ability to inhibit mitochondrial cytochrome-oxidase and hence blocks electron transport, resulting in decreased oxidative metabolism and oxygen utilization [31]. Cyanide determination plays an important role in environmental control and several methods for cyanide determination in aqueous environments have been reported, but, among them, relatively few are based on the use of chromo-fluorogenic chemosensors [32–34].

One chemical characteristic of cyanide is that it is a nucleophilic anion. This particular makes it suitable to test the use of electrophilic pyrylium rings as a reactive centre in reactions coupled to chromogenic events. In fact, the reaction of **7** with cyanide resulted in ring opening and a colour change from magenta to yellow (unpublished results) in a similar fashion as found for the sulfide anion. However, we were interested in take a step further and develop sensory materials for in situ sensing and rapid screening applications and moved to the incorporation of pyrylium reactive derivatives into a polymeric matrix in an attempt to develop sensory materials for cyanide sensing [35].

To achieve this goal the monomer **8** was obtained. First studies confirmed that acetonitrile solutions of **8** changed the colour from yellowish to red upon cyanide addition most likely due to the formation of a cyanoenone derivative upon nucleophilic attack of cyanide to the C2 carbon in the pyrylium ring. In a second step, in order to enhance the applicability of this cyanide-induced chromogenic effect, the probe was covalently anchored into a polymer. The connection between certain types of chromogenic receptors for anions and polymers show certain aspects of interest and the development of new, robust, sensitive sensory materials remains an emerging frontier where there are few examples of chromogenic and fluorogenic polymer-based anion chemosensors [36–38]. Additionally, polymeric films are easily prepared and are ideal candidates for the development of sensory materials for in situ sensing and rapid "naked eye" screening applications. Series of methacrylic copolymer films containing the pyrylium probe were prepared by radical copolymerization with different quantities of the monomer **8**, 2-ethoxyethyl methacrylate (hydrophobic monomer) and 2,3-dihydroxypropyl methacrylate (hydrophilic monomer) (Fig. 7).

The prepared polymers are colourless or pale yellow and changed to red (band centred at 537 nm) in the presence of cyanide in water at pH 11 (Fig. 8). Other anions (Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, SO_4^{2-}, SCN^- and CN^-) induced no significant modifications. Of all the polymeric materials synthesised the best sensing results were obtained with the most hydrophilic films containing a larger percentage of **8** and dihydroxypropyl methacrylate. One particularly attractive feature of the cyanide reactivity with pyrylium rings is that the process is reversible and, for instance, red films saturated with cyanide recover the original yellow colour of the pyrylium-containing films by soaking the polymer into hydrochloric acid solutions. This cyclic process can be repeated at least 10 times without significant degradation of the sensing ability of the sensory polymer.

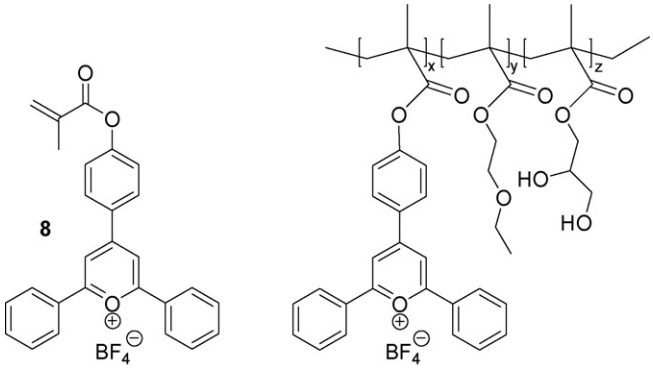


Fig. 7. Structure of monomer **8** and synthesised sensing films.

2.2. Using squaraine derivatives

Squaraine dyes are symmetric conjugated polymethine dyes formed by a central four-member squaric acid ring and, e.g. two substituted aniline moieties at the 1,3-positions of the cyclobutadienyl ring. This class of dye has been extensively used for technical applications (organic solar cells, optical recording media and xerographic photoreceptors) and showed a sharp and intense band in the visible region. From a sensing point of view squaraines usually show remarkable features such as intense absorption ($\log \varepsilon = 5.3$–5.5) in an analytically advantageous wavelength region, at the lower end of the "spectral window", a range suitable for many biological and environmental applications. In this respect, certain squaraine derivatives have been used for the development of chromogenic sensors for cations via covalent linking of cation binding sites with the squaraine scaffolding [39]. However, their use as chromogenic reagents for anion sensing was first reported by us a few years ago. Their use as chromoreactans is based on the presence of the electron-deficient central ring able to undergo nucleophilic attack. Based on this principle chemodosimeters for cyanide and thiols (thiolates) have been developed (see Fig. 9).

Thus, in preliminary studies it was found that bright blue acetonitrile solutions of the chromogenic reagent **9** ($\lambda_{max} = 641$ nm)

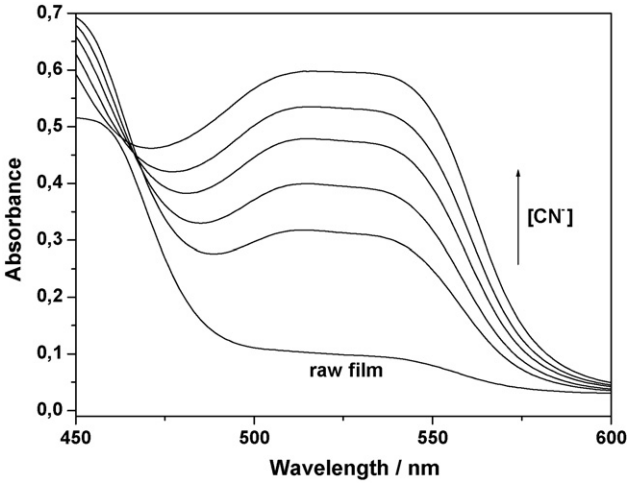


Fig. 8. UV–vis spectra of one of sensory polymers upon exposure to increasing amounts of cyanide in water at pH 11.

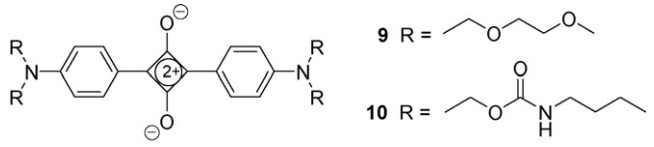


Fig. 9. Molecular structure of the squaraine derivetives **9** and **10**.

became colourless in the presence of cyanide, whereas they remained blue with other anions such as F^-, Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, HSO_4^-, AcO^-, BzO^-, CN^- and SCN^- [40]. This selective bleaching process was attributed to a reaction of the nucleophilic cyanide to the carbon of the four-atom squaraine ring next to the phenyl group (see Scheme 5). This produces both loss of the acceptor character of the ring and the rupture of the electronic delocalization with the consequent disappearance of the squaraine 641 nm band. The compound obtained contains two independent subchromophores that are separated and anchored through a sp^3 carbon. Accordingly, it shows two overlapping bands in the UV spectral region characteristic of the dialkylanilino moiety and the dialkylamino-phenyl-hydroxy-cyclobut-2-enone group. Quantum chemical calculations at the semi-empirical level revealed the existence of the two independent transitions.

Most interestingly, the decolouration process observed for cyanide in acetonitrile also works in buffered water–acetonitrile 80:20 (v/v) at pH 9.5 revealing the potential use of chromogenic reagent **9** for the determination of cyanide in aqueous environments. A detection limit as low as 0.1 ppm was found for cyanide detection using receptor **9**.

In relation to organic molecules, the thiolate anions also react with squaraines such as **9** to produce a bleaching and fluorescence quenching [41]. This effect was also observed in aqueous solutions at neutral pH in the presence of thiol-containing compounds, whereas alcohols, phenols, amines and sulfides produced no colour changes on **9**. Additionally, at this pH neither cyanide, which is protonated in water at neutral pH, gave colour variations. This selective reaction was used for the chromo-fluorogenic detection of thiols such as cysteine (a natural amino acid containing a thiol residue) and other bio-relevant thiol-containing compounds and used, for instance, to the determination of low-molecular mass aminothiols in a complex multicomponent mixture such as human plasma.

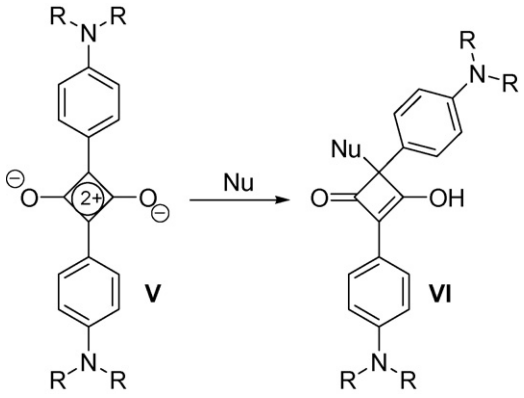
Also relevant was the use of the derivatives **VI** (with Nu = thiolate) for the selective detection of the highly toxic cation Hg^{2+} via Hg^{2+}-triggered formation of the squaraine dye **V** via reaction of this metal cation with **VI** and formation of the corresponding metal–thiolate complex [42].

2.3. Other anion sensing systems

Following a similar approach to that cited above in relation to the use of chemodosimeters, we have recently developed a cyanide chromogenic probe based on a subphthalocyanine dye. Subphthalocyanines are boron-containing macrocycles similar to phthalocyanines but including only three isoindole units, incorporating a 14-π electron aromatic core and a non-planar cone-shaped structure. They show very interesting optical properties and have been extensively employed in a number of fields such as optical storage data, but in contrast, their use as anion chemosensors is rare. We synthesised compound **11**, as a suitable representative of this family of compounds, by reaction of tetrachlorophthalonitrile and boron trichloride following well-known procedures and tested its use as colorimetric probe (see Fig. 10) [43].

11 shows two intense absorption bands centred at 302 nm (Soret band) and at 569 nm (Q band), additionally **11** shows a strong fluorescence even in polar solvents (i.e. in acetonitrile, $\lambda_{em} = 581$, $\Phi_F = 0.26$) with a small Stokes shift. Chromogenic sensing abilities of **11** in acetonitrile showed the elimination of both the Soret and Q bands in the presence of the anions CN^-, F^-, $H_2PO_4^-$ and AcO^- whereas their solutions remained silent in the presence of Cl^-, Br^-, I^-, NO_3^- and HSO_4^-. This bleaching process, indicative of a strong modification of the 14-π electron conjugated system by an anion-induced chemical reaction, increased with time and with the equivalents of the anion added and is most likely due to an anion attack to the π delocalized polyimine framework. Additionally, the presence of twelve electron withdrawing chloride atoms in peripheral positions remarkably increases the reactivity towards ring expansion and breaking of the electronic delocalization.

Moreover, and despite the interesting reactivity of the subphthalocyanine **11** found in acetonitrile, it shows a rather poor selectivity, since four anions F^-, $H_2PO_4^-$, AcO^- and CN^- are able to produce a complete bleaching of the red-pink solutions



Scheme 5. Reaction between squaraine derivatives and nucleophiles.

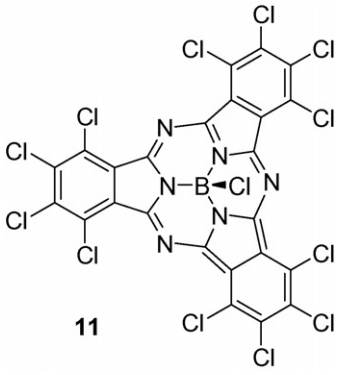


Fig. 10. Molecular structure of chemodosimeter **11**.

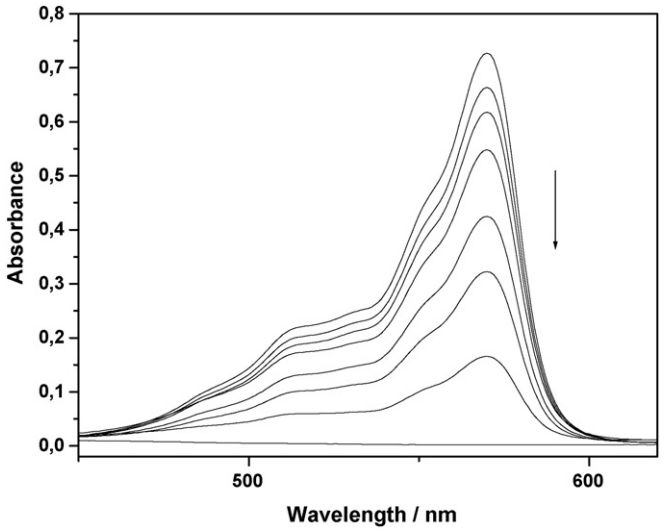


Fig. 11. Changes in the absoprtion spectrum of chemodosimeter **11** in acetonitrile upon addition of increasing cyanide concentrations.

of **11**. However, an interesting feature of this system is that the reactivity, and therefore selectivity, can be handily controlled by a simple modulation of the solvent mixture. Thus, it is known that the nucleophilic character of different species is solvent dependent and that protic solvents decrease the anion nucleophilicity by solvation effects due to hydrogen bonding to the nucleophile's lone pair. A remarkable solvent-induced selectivity enhancement was found using water. By adding 1 vol.% of water to acetonitrile solutions of **11** the bleaching induced by $H_2PO_4^-$ and AcO^- is fully avoided. Up to 3 vol.% of water results in a selective response to fluoride and cyanide, whereas 5 vol.% water-containing acetonitrile solutions of **11** respond selective to cyanide (see Fig. 11). Preliminary analytical tests indicated that acetonitrile–water 1:1 (v/v) (buffered at pH 9.6) solutions of **11** could be used to selectively detect cyanide in the presence of other anions and with detection limits as low as 0.1 ppm.

To finish with this section we would like to show two examples related with the colorimetric and fluorimetric detection of the fluoride anion.

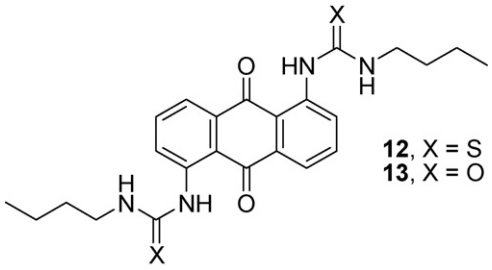


Fig. 12. Chemical structures of anthraquinone-based chemosensors **12** and **13**.

The chemosensors **12** and **13** consist of an anthraquinone core functionalised at 1,5-positions with two thiourea or two urea subunits, respectively (see Fig. 12) [44]. Acetonitrile solution of receptor **12** showed a dramatic colour change from orange to brown (due to the appearance of a new absorption band at 670 nm) upon addition of 10 equivalents of fluoride, whereas the addition of the same quantity of other anions (Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, HSO_4^-, AcO^-, BzO^- and CN^-) induced negligible changes in the UV–vis profile. The behaviour of **13** is less selective and the presence of 100 equivalents of F^-, $H_2PO_4^-$, CN^-, AcO^- and BzO^- anions were able to induce certain colour changes. In a similar fashion as we have seen above with subphthalocyanines dye, change of the solvent also here resulted in an enhancement of both selectivity and sensitivity. Thus, moving from acetonitrile to DMSO solutions of **12** or **13**, only the presence of 2 and 20 equivalents of fluoride, respectively, induced the appearance of the band centred at 670 nm and this behaviour was selective as other anions gave no colour modulations. Bearing in mind the complete studies published recently in relation to chromogenic systems containing urea and thiourea moieties [45], the dramatic colour variation and the presence of the band at 670 nm should be attributed to a urea/thiourea deprotonation process induced by the strongly basic character of the fluoride anion in aprotic solvents [46,47]. Moreover, the absence of isosbestic points in the titration experiments in acetonitrile may be indicative of the existence of two consecutive processes, first a hydrogen bonding interaction at low concentration of fluoride followed by a proton transfer process from the urea/thiourea to the fluoride at larger fluoride concentrations.

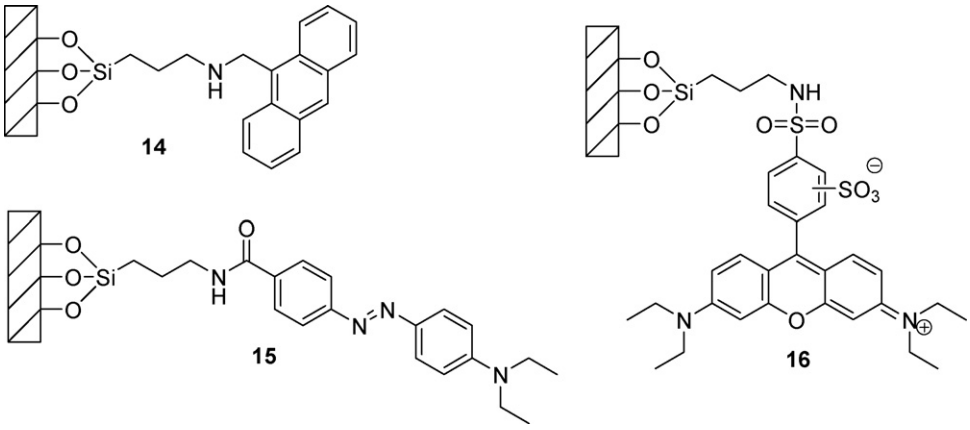


Fig. 13. Structure of the solid chemosensors **14**–**16**.

Another protocol we have followed for the chromo-fluorogenic detection of the anion fluoride uses a pure chemodosimeter approach based on the selective attack of the hydrofluoric acid to a silica matrix grafted with a certain dye [48]. As solid matrix we used mesoporous solids of the MCM-41 family due to its very large specific surface area (ca. 1100 m^2/g) that allows a high degree of functionalisation. Moreover, the presence on this silica support of the porous system additionally provides protection of the signalling dyes.

We prepared the sensory solids **14**, **15** and **16** (see Fig. 13) by simple grafting processes of the MCM-41 mesoporous silica support with different chromogenic and fluorogenic subunits. Fluoride determination with chemodosimeters **14–16** was carried out in acetonitrile–water 70:30 (v/v) buffered to pH 2.5 (0.1 mol dm^{-3} potassium hydrogen phthalate). In a typical procedure 1 mg of the corresponding solid was suspended in 1 mL of the buffer solution and then aqueous samples containing certain amounts of fluoride were added and the suspension stirred for 1 h. The formation of HF at acidic pH induced the rupture of the MCM-41 support and the release of the dye into the solution. After the reaction time the suspensions were filtered and the visible spectra (for **15** and **16**) or emission (for **14** and **16**) of the solution recorded. The release of the dye to the acetonitrile–water solution is proportional to the fluoride concentration in the original sample. The method was applied to the quantitative determination of fluoride in toothpastes with very fine results.

3. Hybrid materials for anion sensing

Recent research interest in our group deals with the development of smart sensory materials based on hybrid organic–inorganic frameworks. Thus, most of the achievements in the field of chemosensing are based on molecular systems and on the simple interaction of the anion with a binding site or reactive centre. This approach sometimes leads to rather unselective chemosensors and interesting examples have been reported in the preparation of ditopic or multitopic ligands and cages in an attempt to enhance selectivity. An attractive alternative to these molecular approaches is to use pre-organised nanoscopic solid state structures in sensing processes [49]. Recent examples suggest that the wise combination of supramolecular models, as those related with recognition/sensing, and nanoscopic supports is leading to new perspectives of applicability of hetero-supramolecular concepts in sensing protocols. This does not refer to the simple anchoring of chemosensors to a solid support but to the search of new effects where the solid scaffolding itself would play a significant role in the recognition/sensing protocol via formation of functional multicomponent ensembles. This would lead to smart sensory materials where the information about the sensing outcome is somewhat encoded in the functionalised solid via combination of a suitable binding sites, additional interactions provided by the solid support and a chromo-fluorogenic event [50,51]. What makes this approach especially attractive is the appearance of new molecular-solid synergic effects that are hardly achievable in molecular-based systems or in nanoscopic solids individually. In this context nice examples have been reported based on the use of nanoparticles [52,53] and mesoporous solids [54,55]. In relation to the sensing of anions we have recently reported the design of sensory materials for the colorimetric and fluorimetric sensing of fatty acids, ATP, citrate and borate.

As particular objectives we seek in this case the design of sensory systems for the chromo-fluorogenic discrimination of certain members of a family of related anions and the development of sensory systems that would work in pure water solutions in order to improve their potential applicability as analytical tools. To do so, we tried to get some inspiration in how nature overcomes the problem of recognition. Thus, for instance, the success of many proteins in binding a certain substrate using rather conventional hydrogen bonding receptors in aqueous media lies in the formation of suitable cavities that shield the active site-substrate complex from competing water molecules. Thus additionally to the certain selectivity induced by the hydrogen bonding receptor, there is an extra discrimination by size and relative polarity that is somehow imposed by the cavity itself where the binding sites are located. Thus, the overall reaction involve two consecutive steps; extraction from water to the pocket and the biological reaction. Although it is almost impossible to achieve the complexity and selectivity presented by proteins and related living systems we took the step of developing bio-inspired systems using similar principles and applied them to the development of sensory materials. We focused our attention on the use of mesoporous supports of the MCM41-type family [56]. They show a narrow and controlled pore size distribution in ordered hexagonal channels with comparatively large pore openings of ca. 25 Å. Additionally, these solids are easily prepared, and functionalised to give final robust materials for sensing purposes. Inner surface functionalisation can be obtained by co-condensation or post-synthetic covalent grafting of organic groups. Moreover, not only mono-functionalisation but successive inclusion of different organic moieties is possible, yielding higher-order hybrid solids that can be seen as a first step toward "biomimetic" nanomaterials [50,51,57].

The development of a hybrid system with selectivity towards long chain carboxylates was one of our first goals [58]. In order to achieve this we used a urea group (as carboxylate binding subunit) electronically coupled to a phenoxazinone scaffolding (as chromogenic and fluorogenic signalling subunit). The spectroscopic properties of this urea-phenoxazinone dye in DMSO or acetonitrile is modulated, for instance, by the presence of carboxylates such as acetate, leading to a deepening of the colour from orange to pink as well as a five-fold enhancement of the fluorescence. However, this system is rather unselective as it responds to any carboxylate and to dihydrogen phosphate in acetonitrile and does not respond to any anion in water. To improve its performance as a sensor we covalently linked the urea-phenoxazinone dye to a UVM-7 material [56] (a MCM-41 type material characterized by a bimodal (MCM-41 type and textural pore system). Additionally, after the first grafting process the solid still possesses many unreacted OH groups, and thus the surface was further functionalised with trimethylsilane giving rise to hydrophobic pockets containing the probes for carboxylate recognition (see Fig. 14). This strategy was assumed to

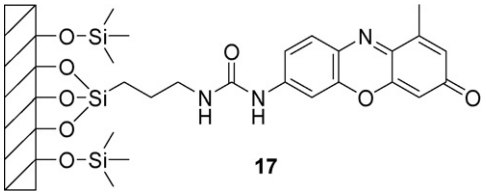


Fig. 14. Structure of the hydrophobic hybrid material **17**.

lead to a "biomimetic" hybrid sensor material where the desired response is only obtained by an appropriate combination of the single components, the anchored probe molecule and the support's environmental properties.

In order to test the sensing capabilities of solid **17** a small amount was put in contact with aqueous solutions containing certain carboxylates. The systems showed a selective response to long chain carboxylates (dodecanoate, tetradecanoate, hexadecanoate, octadecanoate, oleate, linoleate and elaidate), whereas the solid remained silent to shorter carboxylates, inorganic cations, anions and biological species such as triglycerides, cholesterol, bile acids or organic phosphates. The enhancement in the response is evident if ones compare the reactivity of the analogous molecular-based urea-phenoxazinone derivative (see above). Following a similar approach we also have recently achieved a colorimetric discrimination of closely related amines [50,51].

In molecular chemosensors, the signalling process comprises of two steps: (i) the selective coordination of the guest by a suitable binding site and (ii) a transduction step where the process of coordination induces changes in optical or electrochemical parameters. One milestone in this research field is the development of new and effective chemical sensors showing enhanced properties, i.e. selectivity and sensitivity via signal amplification and enhancement of the detection limit of target chemical species. This improved signalling by pre-organisation in solid surfaces has, for instance, been described in nanoparticles and dendrimers [59–61]. Additionally, we have also found a similar improved coordination and signalling in nanoscopic supports such as mesoporous silica functionalised with suitable chemosensor for fluorogenic anion sensing. The strategy involved the grafting of aminoanthracene groups onto UVM-7 as shown in Fig. 15 [62,63]. The solid contains amino subunits as the anion coordinating site and anthracene subunits for both, signalling and provision of additional π-stacking interactions with the target anion ATP. The addition of ATP to acidic aqueous suspensions of the solid resulted in remarkable fluorescence quenching, with association constants for the anion–solid interaction two orders of magnitude larger than that obtained for a similar molecular-based system in solution. The enhancement of response to ATP with the mesoporous solid, compared to the free probe, reveals a cooperative effect related with an effective concentration enhancement and signalling amplification favoured by the regular mesoporosity of the MCM-41 solid.

As we have cited in the introduction of this paper three approaches have been used in the development of optical sensors for anions. Among them, the displacement assay has been extensively employed [64,65]. This approach has several advantages. For instance, the non-covalent anchoring of binding sites and indicator groups allows a large number of combinations to be tested with minimum effort in order to obtain tuned sensing systems. Furthermore, these sensing ensembles usually operate in pure water or water/organic solvent mixtures. However, the displacement approach also has several limitations. One restriction is that the spectroscopic characteristics of the indicator in the molecular ensemble must be different to those in its non-coordinated form. Another disadvantage is that sometimes it requires extensive and time-consuming synthetic efforts to finally obtain somewhat complex receptors. All of these systems are based on the use of molecular anion hosts having in common the presence of binding sites placed in suitable cavities that fit in size and charge with the guest to be coordinated and sensed. These binding pockets have typically been obtained by the use of 1,3,5-trisubstituted 2,4,6-triethylbenzene scaffolds or cages incorporating metal complexes.

Based on the concept that adequately functionalised nanosized cavities in mesoporous solids can mimic active-site cavities found in biological systems (see above), we believe that these materials could be used as binding pockets for the development of novel displacement assays in solid state. The fact that these functionalised-mesoporous solids could be easily obtained overcomes the extensive and tedious synthetic procedures used to obtain the receptors employed in displacement assays in solution.

The protocol is schematically shown in Fig. 16. Suitable nanosized pores are functionalised with appropriate binding sites. The functionalised solid is then loaded with a dye capable of coordinative interaction with the anchored binding sites. In the presence of a target anion displacement of the dye into the solution is achieved and results in colorimetric detection of the guest. UVM-7 was again used as a mesoporous solid support

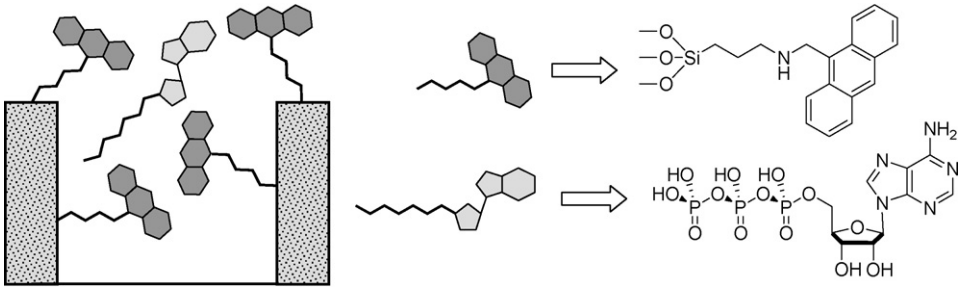


Fig. 15. Schematic representation of the surface of the solid **14** where 30 Å diameter holes filled by aminoanthracene molecules have been represented.

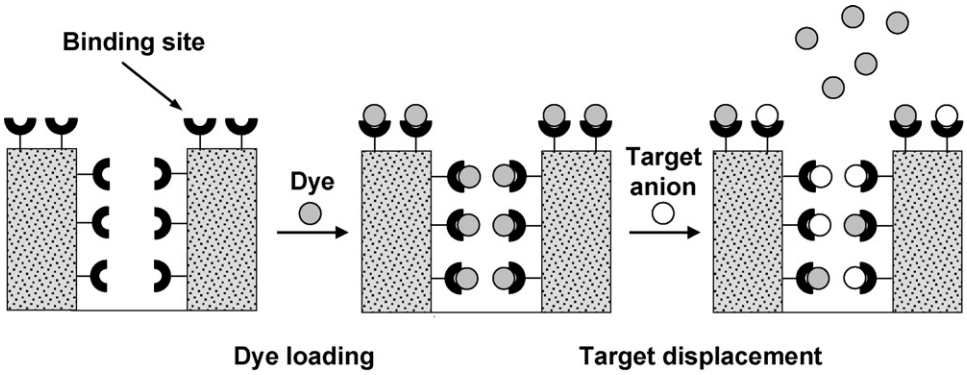


Fig. 16. Schematic representation of the use of functionalised mesoporous materials in colorimetric displacement assays.

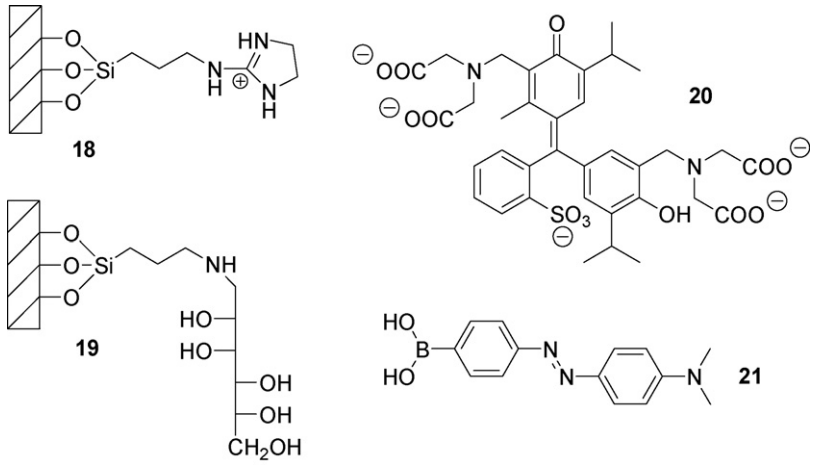


Fig. 17. Chemical structures of hybrid materials **18** and **19** and the dyes used in displacement assays.

and two sensory materials functionalised with guanidinium (**18**) and mannose (**19**) were prepared (see Fig. 17) [66]. The solids synthesized were then charged with methylthymol blue (**20**) and with an azoic dye containing a boronic acid moiety (**21**). These two dyes were capable of giving coordinative interactions with the anchored coordination sites through electrostatic interactions (**18**–**20** ensemble) and boronate ester formation (**19**–**21** ensemble).

The ensemble **18**–**20** was tested in displacement assays in water (buffered at pH 7.5) in the presence of certain carboxylates (citrate, succinate, lactate, malate, acetate, oxalate, propionate, formate, oxalacetate, tartrate, maleate, malonate, glutarate, adipate, pimelate and phthalate). A citrate selective response was found indicating that the binding pockets are capable of recognizing this anion via favourable coordination in relation to other carboxylates (see Fig. 18). A similar functionalised material but using fumed silica which lacks the homogeneous porosity characteristic of mesoporous solids, was prepared but that solid showed a very poor response. This suggested that the presence of cylindrical-shaped pores in the mesoporous solid favoured the spatial proximity between guanidinium subunits resulting in an enhancement of the coordination ability of the binding groups in the nanoscopic binding pockets towards citrate.

In a similar fashion ensemble **19**–**21** presented a selective response towards borate anion in acetonitrile–water 8:2 (v/v) solutions. The selective coordination of borate anion with the hydroxyl moieties presented in solid **19** induced the release of

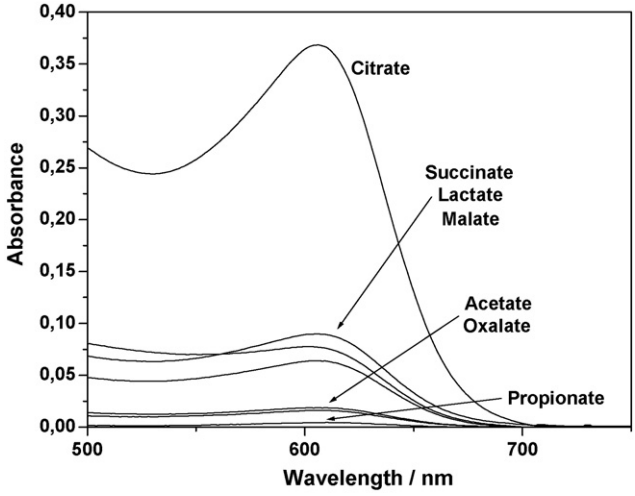


Fig. 18. UV–vis spectra (alter filtering) of the **18**–**20** ensemble in the presence of different carboxylates.

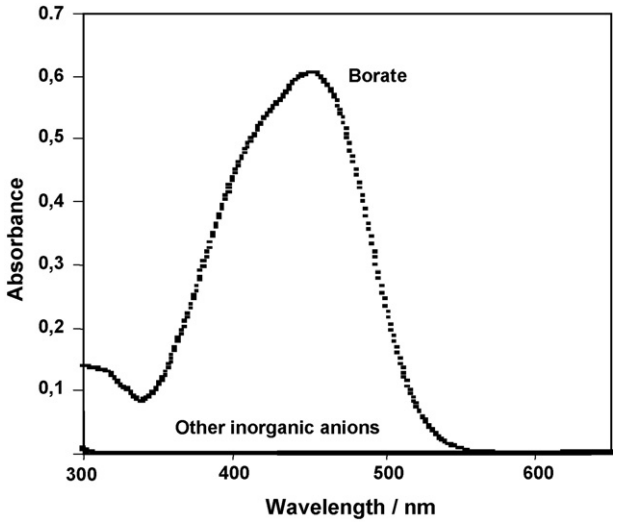


Fig. 19. UV–vis spectra (alter filtering) of the **19**–**21** ensemble in the presence of different inorganic anions.

dye **21** into the solution allowing the colorimetric detection of this anion of environmental importance (see Fig. 19).

4. Future perspectives

We have reported here some recent advances in anion detection using colorimetric and fluorimetric systems recently developed in our research group. Some of them are based on the so called chemodosimeter approach where anion selectivity is achieved via anion-induced chemical reactions. This together with the "binding site-signalling subunit" and "displacement assays" are the commonly used approaches to develop anion sensing protocols. A quite common problem that somehow limits the real application of these systems is the fact that many developed optical sensors display sensing properties in non-aqueous solvents. How to overcome this limitation together with the search for new, advanced and original protocols for optical anion sensing are, to our viewpoint, some of the ideas that might drive the anion sensing research in the following years. In this respect we have also shown certain advances in the design of chromogenic and fluorogenic sensory materials using a combination of supramolecular models and nanoscopic supports and the formation of functional organic–inorganic multicomponent ensembles. This approach using hybrid supramolecular systems for sensing purposes is still in its infancy but new advances will occur in the near future. We believe that very promising results will rise from the blending of the chemistry of nanoscopic solid materials with supramolecular functionalities applied to the development of new smart sensory materials.

Acknowledgements

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