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Cyanide Sensing with Organic Dyes: Studies in Solution and on Nanostructured Al_2O_3 Surfaces

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Abstract: The synthesis of two new azo phenyl thiourea compounds and their optical response to different anions is reported herein. Solution studies in methanol indicate that cyanide induces a colour change in these dyes (whereas no changes are observed in the presence of other anions, such as F^-, Cl^-, Br^-, CH_3COO^-, $H_2PO_4^-$, HSO_4^-). Interestingly, in DMSO these dyes are responsive not only to cyanide, but also to fluoride, acetate and dihydrogen phosphate. Each of these anions induces a different colour change. In the second part of the paper, we report the attachment of one of these dyes onto nanostructured TiO_2 and Al_2O_3 films. The stability of these sensitised films to pH was studied and we concluded that the sensitised Al_2O_3 films are more robust, and hence, better than the TiO_2 for anion sensing. The dye-sensitised Al_2O_3 films were immersed in solutions of different anions and their response studied. The films can detect cyanide down to 3 ppm in aqueous solution with relatively good selectivity over other anions.

Keywords: anions · cyanide detection · sensitizers · sensors · thin films

Introduction

The recognition and sensing of anions has received considerable attention over recent years.[1–7] Part of this interest stems from the important roles anions play in biological processes (e.g., phosphates).[8] In addition, there is interest in finding better and more efficient ways of detecting anions that can be potentially harmful to the environment or human health. One such anion is cyanide, which is lethal to humans at concentrations of 0.5–3.5 mg per kg of body weight.[9] Consequently, the presence of this anion in drinking water (e.g., as a result of spillage from industrial waste or mining activities) can pose a very serious risk to human health. It is therefore evident that reliable and efficient ways of detecting the presence of cyanide in water are needed.

Several methods have previously been developed to detect cyanide by using a wide diversity of experimental protocols and detection techniques.[10–18] Methods based on anion-induced changes of the optical properties (either absorption or emission) of a receptor are especially attractive. Recent examples that use this approach have been reported by the groups of Geddes,[19–21] Martinez-Mañez,[22–25] Palomares[26,27] and Raymo[9,28] amongst others.[29–33] In spite of these developments there are still relatively few examples of selective probes for cyanide owing to high interference from other anions, in particular, fluoride.[33,34] Another drawback with most of the current methods is that the detection needs to be carried out in organic solvents (or mixtures of organic solvents and water), which limits their application to the analysis of “real” samples that are often aqueous solutions. In addition, in most of the current methods the chemical sensors have to be in solution to perform sensing. Only in a few cases has sensing been reported to take place over a surface or film,[27,35,36] which is very convenient for quick and easy detection of the anion.

Herein, we report the synthesis of two new azo phenyl thiourea compounds and their ability to selectively detect cyanide. The first studies we present have been carried out in solution (in methanol and DMSO), which show that these dyes are indeed sensitive to the presence of anionic species. The second part of our investigations focused on incorporating one of these dye compounds onto nanostructured semiconducting surfaces to generate cyanide-sensing films.

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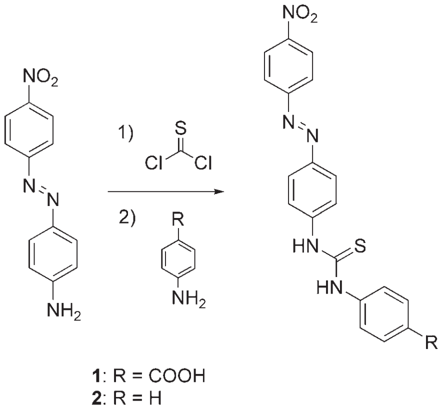
Results and Discussion

Synthesis of thiourea dyes 1 and 2: 4-Nitrophenylazo derivatives have previously been used as chromogenic subunits in the development of receptors for anion sensing.[37] These systems contain an acceptor nitro-phenyl moiety connected to a donor atom (N or O) through a conjugated azo system. Modification of the nature of the donor through hydrogen bonding can result in a redshift in the charge-transfer (CT) band in the UV-visible region, and consequently, in a change in colour. With this in mind, compounds **1** and **2** were prepared (see Scheme 1). The synthesis was carried out by treating the commercial dye Disperse Orange 3 (4-(4-nitrophenylazo)aniline) with thiophosgene, followed by treatment with the corresponding amine, either 4-aminobenzoic acid or aniline.



Scheme 1.

These compounds were characterised by spectroscopic and analytical techniques. The ^{1}H and ^{13}C NMR spectra of both samples were consistent with the proposed formulations. The integrations and multiplicity of the aromatic resonances in the ^{1}H NMR spectra were indicative of the presence of both aromatic rings in **1** and **2**. A resonance in the ^{13}C NMR spectra of both samples at $\delta = 180$ ppm was assigned to the thiourea carbon. The formulations of these two molecules were confirmed by FAB^{+} mass spectrometry (which gave a molecular peak at 422 amu for **1** and at 378 amu for **2**) and elemental analyses.

Studies of the anion–dye interactions in solution: The anion sensing properties of **1** and **2** were studied in solution by using methanol and DMSO as solvents. An intense band for the $\pi \rightarrow \pi^*$ transition of the 4-nitroazophenyl chromophore appears at 390 (in methanol) and 412 nm (in DMSO) for **1** and at 414 nm for **2** (in DMSO). The anions selected for these studies were F^-, Cl^-, Br^-, CH_3COO^-, $H_2PO_4^-$, HSO_4^- and CN^-. A solution of **1** in methanol (0.5 mM) was treated with a fixed amount of the different anions (30 equiv, added as tetrabutyl ammonium salts). As shown in Figure 1, only the addition of CN^- caused a change in the UV-visible absorption spectrum of the dye (the λ_{max} of the dye shifted from 390 to 414 nm). This was also evident by naked-eye inspection: a colour change from pale orange to red/orange was only observed upon addition of cyanide (Figure 2).

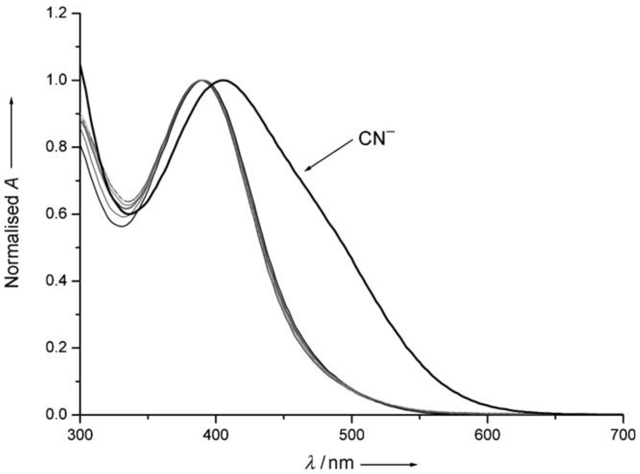


Figure 1. Normalised UV/Vis spectra of a 0.5 mM solution of **1** in MeOH upon addition of different anions (30 equiv).

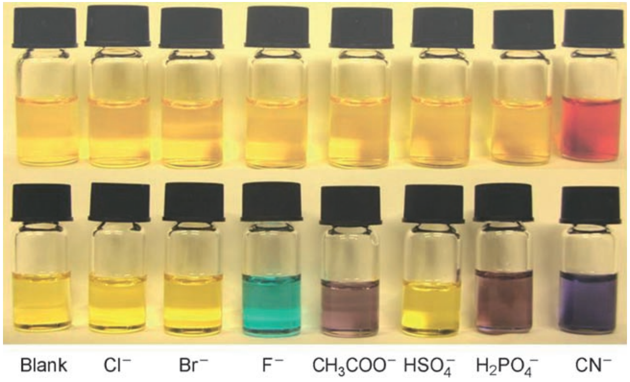


Figure 2. Photograph of solutions of **1** with different anions in methanol (top) and DMSO (bottom).

Once the selectivity of the dye for cyanide sensing was established, it was of interest to determine its sensitivity towards this anion. Titration of a 0.5 mM solution of **1** with cyanide showed a progressive shift from 390 to 414 nm (Figure 3).

Since the optical properties of azo dyes can change as a function of the solvent in which they are dissolved, analogous studies to those described above were carried out in DMSO. In this case, more striking colour changes were observed, not only for cyanide, but also for other anions (Figure 2). Addition of CN^- or F^- to a solution of **1** in DMSO, changed its colour from pale orange to dark violet and blue, respectively, whereas CH_3COO^- and $H_2PO_4^-$ induced a change to dark red/purple. In contrast, no changes in colour were detected upon addition of other anions, such as Cl^-, Br^- or HSO_4^-.

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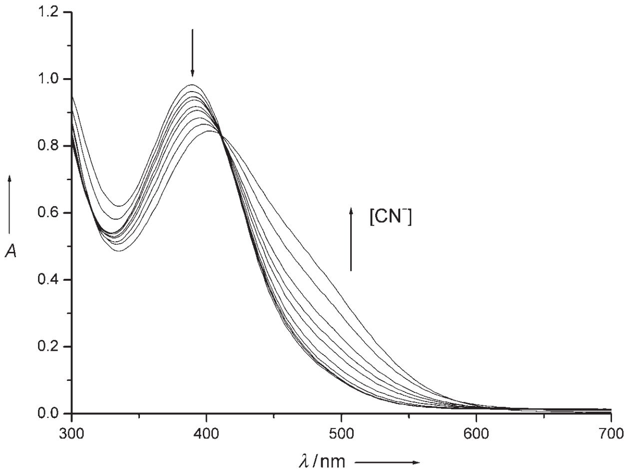

Figure 3. Changes in the UV/Vis spectra upon the addition of increasing amounts of cyanide to a 0.5 mM solution of **1** in methanol. With this data a log$K$ value of 2.02 ± 0.13 was obtained.

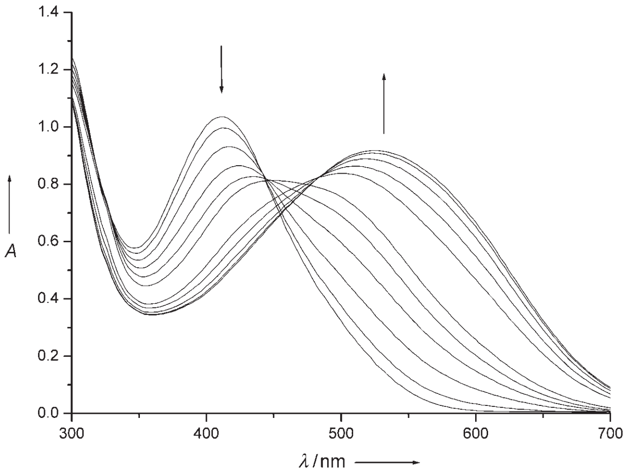

Figure 4. Changes to the spectrum of **1** upon the addition of increasing amounts of cyanide, showing the λ_{max} shift from 412 to 542 nm. The spectra were obtained by using a 0.5 mM solution of **1** in DMSO.

To investigate quantitatively the changes observed in DMSO upon addition of CN^-, F^-, CH_3COO^- and $H_2PO_4^-$, a series of titrations using UV-visible spectroscopy were carried out. An example of the titration curves obtained upon addition of increasing amounts of cyanide to **1** is shown in Figure 4. The changes observed in the absorption spectrum of **1** suggest that three different species are present, the proportions of which depend on the amount of cyanide added.

In the absence of anion, compound **1** in DMSO has a λ_{max} value of 412 nm. Upon addition of one equivalent of cyanide, a second species with maximum at around 460 nm (the peak is too broad to determine the λ_{max} value accurately) appears. Increasing amounts of cyanide yield a third species with a λ_{max} of 542 nm, which is the compound associated with the dark blue/violet colour of the final solution. The origin of the colour changes and differences in the behaviour of **1** in methanol and DMSO are not immediately evident. Previous studies with urea- and thiourea-containing chromophores have shown that, in principle, anions can induce changes in colour through two distinct processes: hydrogen bonding or deprotonation of the N–H groups. These two processes are highly dependant on the solvent in which the studies are carried out and the basicity of the anions under study. To investigate this further, several studies were carried out.

First, analogous dye **2** (see Scheme 1), which lacks a terminal COOH group, was prepared and its optical response to anions was studied. In DMSO, by naked-eye inspection, this dye behaves largely as compound **1**. However, closer inspection of the absorption spectra upon the addition of increasing amounts of the corresponding anions revealed an isosbestic point, which indicated that the conversion of the initial product to the final blue-purple compound does not go via a detectable intermediate (see Figure 5 for an exam-

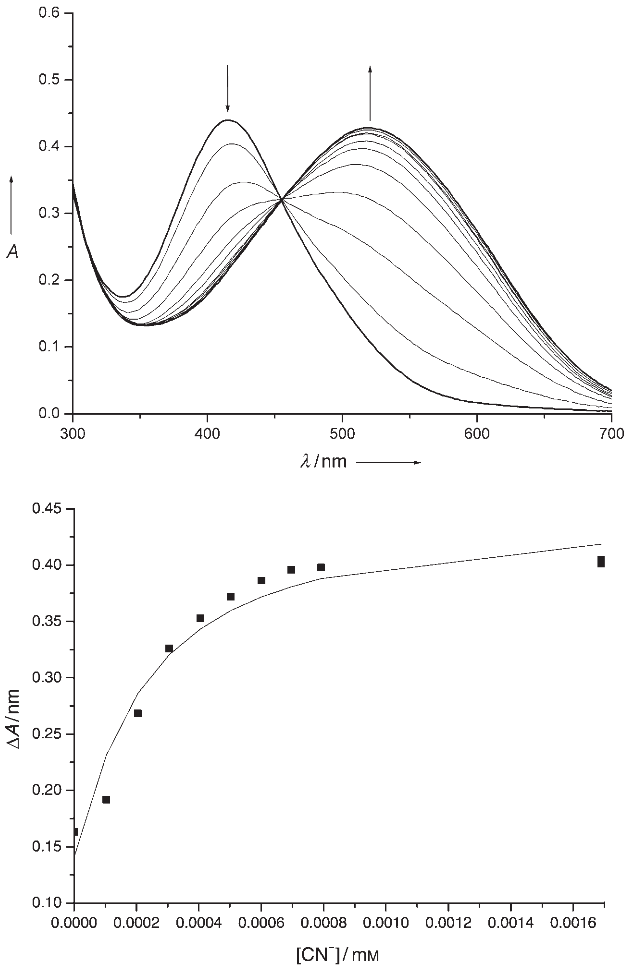

Figure 5. a) Changes in the spectrum of **2** upon the addition of increasing amounts of cyanide, showing the λ_{max} shift from 414 to 520 nm. The spectra were obtained by using a 0.1 mM solution of **2** in DMSO. b) Plot showing the change in absorbance of **2** at 414 nm (as a ΔA) with the addition of increasing amounts of cyanide.

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ple in which cyanide was used as the titrant; plots for the titrations with other anions can be found in the Supporting Information).

From the plot of ΔA versus equivalents of cyanide added (Figure 5b) the overall equilibrium constant of the system was determined to be $\log K = 4.2 \pm 0.15$, which, as discussed below, corresponds to the deprotonation of the thiourea group by the corresponding anion.

From these results, it is clear that the major colour changes of **1** upon addition of anions cannot be the result of simple deprotonation of the carboxylic acid of the dye because almost the same colour changes were observed for both **1** and **2** when cyanide was added. However, it is likely that the intermediate species observed by UV-visible spectroscopy in the titration of **1** (but not in **2**) with cyanide ($\lambda_{max} \approx 460$ nm.) is indeed associated to the deprotonation of the carboxylic acid group in **1**.

^{1}H NMR spectroscopic studies were carried out to gain some insight into the structural changes of the dyes upon addition of different anions (namely, Cl^-, CH_3COO^-, $H_2PO_4^-$ and F^-; cyanide was avoided owing to its toxicity and the fact that in DMSO solution its behaviour was analogous to that of fluoride). The corresponding anions (30 equiv) were added to solutions of **1** in [D$_6$]DMSO and the ^{1}H NMR spectra were measured. Upon the addition of the anions, the orange dye solution retained its original colour for chloride, turned red for acetate and phosphate, and blue for fluoride. The ^{1}H NMR spectra of the solutions that contained fluoride and acetate showed very broad peaks, whereas for chloride and phosphate sharp and clearly identifiable peaks were observed.

The spectrum of the initial anion-free solution of **1** showed six doublets between $\delta = 7.69$ and 8.44 ppm, which corresponded to the protons of the three aromatic rings (two signals for each) and two singlets at $\delta = 10.44$ and 10.49 ppm, which corresponded to the protons of the thiourea. Upon addition of chloride to this solution, the aromatic protons of **1** appeared to be slightly shifted, but the original pattern was retained; the resonances associated with the thiourea NH protons shifted to $\delta = 11.70$ and 11.83 ppm, respectively, which suggested the formation of hydrogen bonds between the chloride and the dye. In contrast, addition of dihydrogen phosphate to **1** (which produces a colour change to red) generated greater changes in the ^{1}H NMR spectrum; two of the doublets associated with the aromatic protons of **1** and the two NH thiourea resonances disappeared. This clearly indicates more important changes to the structure of **1** than simple hydrogen-bonding interactions.

Based on the previous work reported by the groups of Fabrizzi[39–41] and Gale[42–44] for similar systems to that presented herein, the striking change in colour observed for solutions of **1** and **2** in DMSO can be associated with deprotonation of the NH groups of the thiourea. In the first step and with the less basic anions, such as CH_3COO^- and $H_2PO_4^-$, only one of the NH groups of the thiourea is deprotonated (in the case of **1** the carboxylic acid should also be deprotonated) to yield a red-coloured conjugated species. With anions such as fluoride or cyanide, it is likely that the second NH group is also deprotonated to yield a fully conjugated species with an intense blue-violet colour. Our spectroscopic observations (both by ^{1}H NMR and UV/Vis spectroscopies) are consistent with this type of deprotonation process.

Sensitivity and detection limit in solution: Once the anion selectivity of **1** and **2** in MeOH and DMSO was established, it was of interest to determine the sensitivity and the detection limit of the system. The former can be defined as the rate at which the absorbance changes upon addition of the analyte, namely, d(A)/d[anion]. On the other hand, the detection limit depends on the instrumentation (i.e., the minimum change in absorbance that can be reliably measured spectroscopically, which is 0.01 in this case) and on the sensitivity of the dye (as defined above). By using these two parameters, the detection limit can then be calculated as 0.01/sensitivity. With the titration data shown in Figures 3, 4 and 5, it was possible to determine the sensitivity and detection limit of **1** (in MeOH) to cyanide, and of **1** and **2** (in DMSO) to cyanide, fluoride, acetate and phosphate. These results are summarised in Table 1.

Table 1. Detection limit (defined as 0.01/sensitivity in which sensitivity = d(A)/d[anion]) in ppm for **1** and **2** for different anions. In the case of **1** in MeOH the detection limit is only reported for cyanide because no optical changes were detected with other anions.

Dye	Solvent	CN^- [ppm]	F^- [ppm]	CH_3COO^- [ppm]	$H_2PO_4^-$ [ppm]
1	MeOH[a]	8.00	–	–	–
1	DMSO[a]	0.95	0.33	0.92	0.57
2	DMSO[b]	0.06	0.23	0.17	1.04

[a] Concentration of the dye was 0.5 mM. [b] Concentration of the dye was 0.1 mM.

Dye sensitised TiO_2 and Al_2O_3 films: Once the anion-sensing properties of **1** were established in solution, it was of interest to incorporate this dye onto nanostructured semiconducting films. The advantages of doing this is that dip-in sensing is then possible (which is much more practical), and as we and others have previously demonstrated,[26,27] receptors that are not soluble in water (as is the case with **1**) once supported onto films, can be exposed to aqueous solutions of the analytes to be measured.

Compound **1** was first supported on a TiO_2 film by immersing it in a solution of the dye, which yielded an orange film with a λ_{max} value of 366 nm. The film was then exposed to aqueous solutions of various anions (the same as those used in solution) and the optical changes of the film investigated. An initial qualitative naked-eye study indicated that the film only changed colour (to a darker orange-red) in the presence of cyanide. This behaviour is analogous to that observed for **1** in methanol (see above). However, a closer inspection of the system showed that in the presence of cyanide, not only does the adsorbed dye change colour, but it also desorbs from the film. This was confirmed by measuring

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the UV-visible absorption spectrum of the sensitised TiO_2 films in the presence of increasing amounts of cyanide. The intensity of the λ_{max} band decreased with increasing amounts of the anion; in addition the aqueous solution in which the film was immersed, turned orange, which indicated that the dye was desorbing.

It is likely that this problem is caused by an increase in the pH (more basic) of water upon the addition of anions. To investigate this hypothesis, the **1**-sensitised film was immersed in aqueous solutions of different acidity (namely, pH 5 or 9) and left in such solutions for some time. As shown in Figure 6, a constant decrease in the intensity of the λ_{max} of the film was observed at pH 9 with time. Considering that this pH value can be easily reached in unbuffered aqueous solutions of anions, it was concluded that TiO_2-sensitised films were not suitable for sensing anions with this dye.

Therefore, we investigated whether Al_2O_3 could be suitable as nanostructured support for sensing anions with **1**. Al_2O_3 is of particular interest because it has a basic point of zero charge relative to TiO_2 (at pH ≈ 4 for TiO_2 and pH ≈ 9 for Al_2O_3).[38,45] Hence, at pH values below ≈ 9 the Al_2O_3 surface will be positively charged, which allows strong interaction with the carboxylate group of the dye. The result of this is that **1** does not easily desorb from Al_2O_3 at $pH < 9$ (in contrast with TiO_2 in which the surface is only positive below pH ≈ 4, and therefore, the dye desorbs at neutral or basic pH values).

The methodology to prepare the mesoporous Al_2O_3 films is given in the Experimental Section. Similar dye loading was observed for these films compared to TiO_2.

As can be seen in Figure 6, dye-sensitised Al_2O_3 films (using **1**) were indeed much more stable towards desorption at basic pH values, even after leaving the film immersed in the basic solution for 20 min.

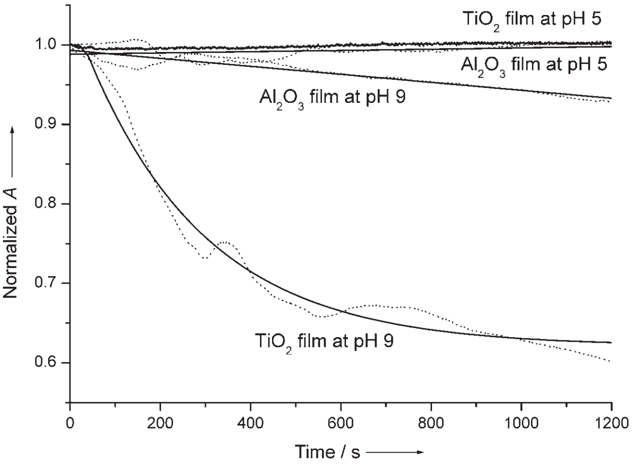

Figure 6. Plot showing the reduction in intensity of the λ_{max} absorption for the $1/TiO_2$ and $1/Al_2O_3$ films as a function of pH.

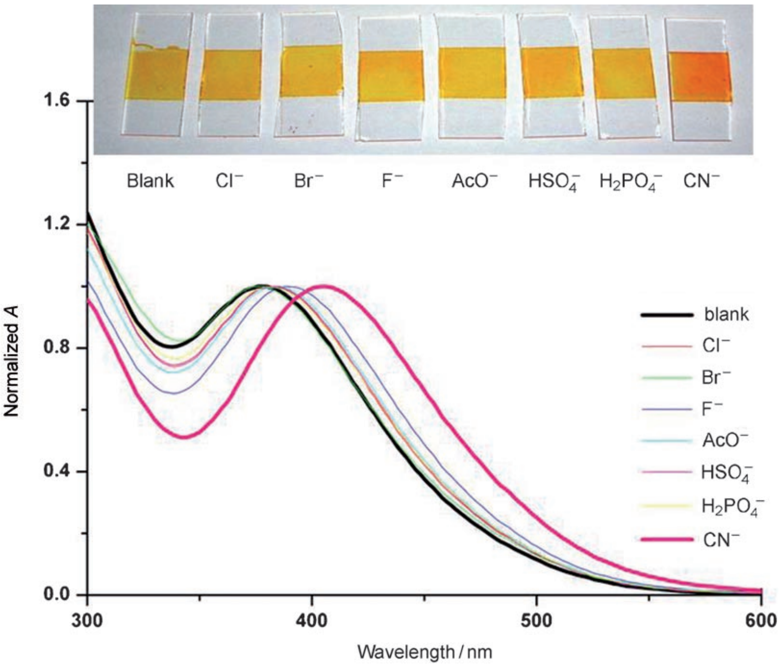

Figure 7. Normalised absorption spectra of $1/Al_2O_3$ films immersed in 5 mM aqueous solutions of different anions.

Anion response of Al_2O_3-sensitised films: Having established the stability of the $1/Al_2O_3$ film towards desorption under basic conditions, its response to different anions was studied by UV-visible spectroscopy. The film was immersed in 1 and 5 mM aqueous solutions of different anions (namely, F^-, Cl^-, Br^-, CH_3COO^-, $H_2PO_4^-$, HSO_4^- and CN^-) and the absorption spectra recorded. As shown in Figure 7, immersion of the film in a 5 mM solution of cyanide caused a λ_{max} shift of the sensitised film from 376 to 406 nm. This shift was also visible by naked eye inspection of the film (see inset in Figure 7); the colour changed from yellow/orange to red/orange.

To establish the sensitivity of $1/Al_2O_3$ to cyanide and the detection limit of the system, the absorbance of the film at different cyanide concentrations was recorded (Figure 8). Plotting ΔA versus [CN] allowed us to calculate the sensitivity (namely, $d(\Delta A)/d(CN)$) to be 0.3 mM^{-1} and the detection limit to be 2.6 ppm (using 0.01/sensitivity as explained above).

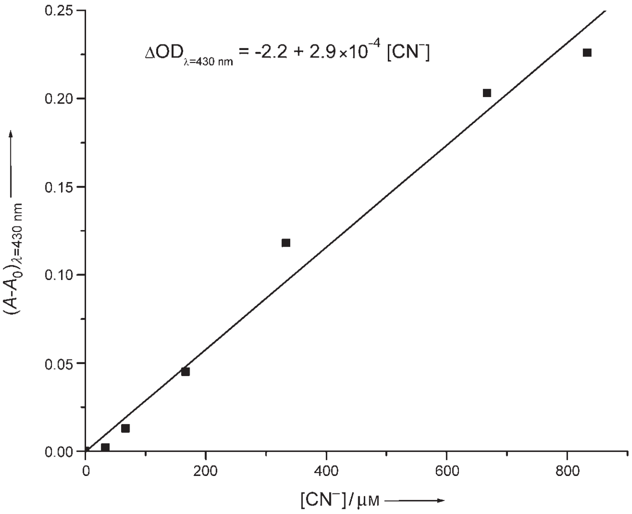

Figure 8. Normalised absorption spectra of **1**/Al_2O_3 films immersed in aqueous solutions of cyanide at different concentrations.

Conclusions

Two new dyes have been prepared and their optical response to anions has been studied both in solution and supported onto Al_2O_3 nanostructured films. In solution, the colour changes displayed by the dye strongly depend on the solvents employed. In methanol, the dye only changes colour in the presence of cyanide (with a detection limit of 8 ppm); even when a large excess of the other anions was used, no colour changes were observed. In DMSO, not only CN^- induces colour changes (in this case to dark purple), but also F^- (to blue), $CH_3COO^-$and $H_2PO_4^-$ (both to violet/red). Our spectroscopic data, together with recent reports in the literature from the groups of Fabrizzi[39–41] and Gale,[44] strongly suggests that the origin of the colour changes is not a simple hydrogen-bonding interaction, but a process that involves deprotonation of the thiourea NH groups.

Compound **1** was then supported on nanostructured Al_2O_3 films and its optical properties studied. These sensitised films were stable to desorption over a wide pH range (in contrast with the behaviour observed with TiO_2 films). Immersion of the **1**-sensitised Al_2O_3 film in an aqueous solution of cyanide induced a colour change that can be used for the detection of cyanide down to 2.6 ppm. These easy-to-use films also showed a good degree of selectivity (although these will need further improvements in future work).

Experimental Section

Materials and instrumentation: Solvents were dried from the appropriate drying agent, degassed and stored under nitrogen. All commercially available starting materials were purchased from Aldrich and not further purified unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded by using a Bruker Avance 400 Ultrashield NMR spectrometer with TMS as the internal reference. IR spectra were recorded by using a Research Series FTIR instrument as KBr disks in the range from 4000 to 500 cm^{-1}. UV/Vis absorption spectra were monitored at room temperature by using a Thermo Genesys 10 UV/Vis spectrophotometer. Elemental analyses were carried out at the London Metropolitan University. The association constants were calculated from non-linear curve fitting of the spectroscopic data by using a 1:1 binding model with the SPECFIT program.[46]

Synthesis of 1: *Step 1*: Disperse Orange 3 (2.12 g, 8.74 mmol) was dissolved in THF (150 mL), and thiophosgene (1.35 mL, 17.58 mmol) was added. The reaction mixture was heated to reflux and stirred for 1 h while argon was bubbled through the solution. All volatiles were evaporated under reduced pressure to yield 4-nitroazobenzene-4′-isothiocyanate as a red solid. This was used in the next step without further purification.

Step 2: 4-Carboxyaniline (1.0 g 7.28 mmol) was dissolved in dried THF (50 mL). 4-Nitroazobenzene-4′-isothiocyanate (2.480 g 8.74 mmol; obtained in the first step) was dissolved in THF (100 mL) and added to the solution of 4-carboxyaniline. The reaction mixture was heated at reflux for 6 h under N_2 and stirred at room temperature for a further 12 h. The solid was removed by filtration and the solvent evaporated to yield an orange-red solid. The crude solid was washed with methanol to yield the pure product as an orange solid (1.84 g, 60%). ^1H NMR (400 MHz, [D_6]DMSO): $\delta=8.44$ (d, J=9.2 Hz, 2H), 8.07 (d, $J=9.2$ Hz, 2H), 7.99 (d, $J=9.2$ Hz, 2H), 7.93 (d, $J=8.4$ Hz, 2H), 7.84 (d, $J=9.2$ Hz, 2H), 7.69 ppm (d, $J=8.4$ Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta=179.5$, 167.4, 155.8, 148.6, 148.5, 144.3, 143.9, 130.5, 126.6, 125.6, 124.5, 123.8, 123.1, 122.5 ppm; UV/Vis: λ_{max} (ε)=376 nm (8,300 $M^{-1}\,cm^{-1}$); MS-(FAB+): *m/z* (%): 422 (100) $[M+1]^+$; elemental analysis calcd (%) for $C_{20}H_{15}N_5O_4S$: C 57.00, H 3.59, N 16.62; found: C 57.25, H 3.72, N 16.42.

Synthesis of 2: Aniline (0.082 g, 80 μL 0.88 mmol) was dissolved in dried THF (10 mL). 4-Nitroazobenzene-4′-isothiocyanate (0.300 g, 1.06 mmol; obtained as described in the synthesis of **1**) dissolved in dried THF (10 mL) was added and the mixture was heated at reflux for 2 h under N_2. The mixture was then allowed to cool, the solid was removed by filtration and the solvent was evaporated to yield an orange-red solid. The crude solid was washed with methanol to yield the pure product as an orange solid (0.17 g, 50%). ^1H NMR (400 MHz, [D_6]DMSO): $\delta=10.28$ (s, 1H), 10.16 (s, 1H), 8.43 (d, $J=8.8$ Hz, 2H), 8.06 (d, $J=8.8$ Hz, 2H), 7.97 (d, $J=8.8$ Hz, 2H), 7.84 (d, $J=8.8$ Hz, 2H), 7.51 (d, $J=8.0$ Hz, 2H), 7.36 (t, $J=8.0$ Hz, 2H), 7.16 ppm (t, $J=8.0$ Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta=179.7$, 155.8, 148.6, 148.3, 144.7, 139.6, 129.0, 125.6, 125.3, 124.4, 124.1, 123.8, 122.9 ppm; UV/Vis: λ_{max} (ε)=412 nm (ε=47,300 $M^{-1}\,cm^{-1}$) MS (FAB+): *m/z* (%): 378 (100) $[M+1]^+$; elemental analysis calcd (%) for $C_{19}H_{15}N_5O_2S$: C 60.46, H 4.01, N 18.56; found: C 60.34, H 4.30, N 18.90.

Preparation of mesoporous nanocrystalline TiO_2 films: Mesoporous nanocrystalline films consisting of anatase TiO_2 particles (15–25 nm in size) were prepared as follows: titanium isopropoxide (40 mL) was mixed with glacial acetic acid (9.1 g) under a nitrogen atmosphere and stirred for 10 min. The mixture was then poured into a conical flask that contained 0.1 M aqueous nitric acid (240 mL) at room temperature and it was subsequently stirred at 80 °C for 8 h. The TiO_2 colloidal was filtered by using a 0.45 μm syringe filter and then autoclaved at 220 °C for 12 h. The colloids were re-dispersed with a 2 min cycle burst from an LDU Soniprobe horn, as reported previously.[26] The solution was then concentrated to 12.5% (in TiO_2 weight) on a rotary evaporator by using a membrane vacuum pump at 45–50 °C. Carbowax 20000 (50% TiO_2 by weight) was added and the resulting paste was stirred slowly overnight before distilled water (50:50 w/w to the TiO_2 paste) was added to dilute the TiO_2 paste for ensuring a thin film. The mixture was stirred slowly overnight prior to film deposition to ensure homogeneity and prevent trapped air bubbles. The paste was spread on the FTO substrates using a glass rod and 3M adhesive tape was used as spacer. After drying in air, the film was sintered at 450 °C for 30 minutes in a furnace. The resulting film thickness, using one layer of 3M adhesive tape, was of 1.4 ± 0.1 μm (measured by Alpha 200 Profilometer).

Preparation of mesoporous nanocrystalline Al_2O_3 films: Colloidal aluminium oxide (50 nm, Alfa Aesar) was diluted with distilled H_2O (50:50) and hydroxypropyl cellulose (2 wt%, 370,000 g mol^{-1}; Sigma Aldrich)

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was added. The mixture was stirred for a week to allow the polymer to dissolve completely prior to film deposition, which ensured homogeneity and that no air bubbles were trapped within the film. The Al_2O_3 paste was doctor bladed onto the microscope slide with one layer of Scotch Tape. The film was dried at room temperature for about 20 min, and then calcined at 400 °C for 30 in. Typical Al_2O_3 films were (3.8 ± 0.2) µm thick. Films were recalcined for 20 min at 400 °C before dye sensitization.

The nanocrystalline Al_2O_3 material was further analysed by X-ray powder diffraction, which showed that the structure of the alumina was γ-Al_2O_3. This was carried out by using a Bruker Advance D8 instrument, which measured at a 2θ range of 20 to 80° with $Cu_{K\alpha}$ radiation.

Sensitising the TiO_2 films: Compound **1** was adsorbed onto a TiO_2 film by soaking the film in a solution of the dye (1 mM) in a 1:1 mixture of acetonitrile/*tert*-butanol at room temperature overnight. A yellow **1**/TiO_2 film was obtained. The dye loading on the film was determined to be 159 $nmol\,cm^{-2}$.

Sensitising the Al_2O_3 films: Compound **1** was adsorbed onto a 4 µm-thick Al_2O_3 film by soaking the film in a solution of the dye (0.1 mM) in a 1:1 mixture of acetonitrile/*tert*-butanol at room temperature overnight. A yellow **1**/Al_2O_3 film was obtained. The dye loading on the film was determined to be 152 $nmol\,cm^{-2}$.

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