Surfactant-assisted chromogenic sensing of cyanide in water†

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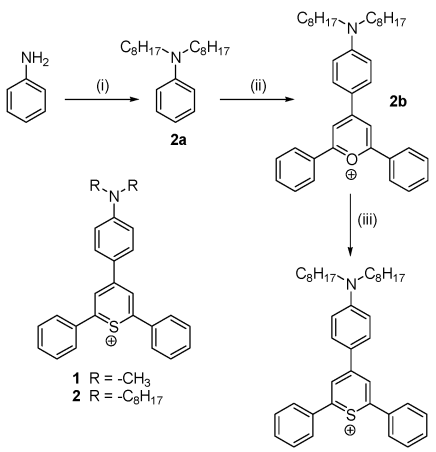
Received (in Montpellier, France) 15th May 2009, Accepted 11th June 2009
First published as an Advance Article on the web 26th June 2009
DOI: 10.1039/b909705h

Chromogenic cyanide recognition in water was achieved by the use of a hydrophobic dye in micellar containers.

Anion detection by chromogenic chemosensors and reagents is an area of emerging interest in the field of supramolecular and anion chemistry.[1] However, despite remarkable advances, there are a large number of chromogenic probes that are reported to display sensing features only in organic solvents. In fact, the preparation of probes for certain target anions in pure water is still a challenge, since many receptor–anion interactions suffer from strong solvation effects that impose a highly effective energetic barrier that inhibits sensing paradigms from occurring in aqueous solution.[2,3] From the different protocols that can be followed to achieve this goal, we believe that the use of paradigms relying on a selective anion reaction with a certain substrate in a chemodosimeter fashion are especially appealing.[4] Based on these concepts, and also due to our interest in the development of chromogenic anion probes,[5] we report herein the use of a thiopyrylium derivative for the chromogenic sensing of cyanide. Highly selective optical detection of cyanide to ppm levels was obtained in pure water containing a neutral surfactant.

In spite of the fact that the cyanide anion is highly toxic to living organisms, the use of cyanide salts in fields such as gold mining, electroplating, resins, synthetic fibers, metallurgy, *etc.* remains widespread.[6] Cyanide can also be found in foods such as bitter almonds, cassava roots, *etc.* Due to its high toxicity and extensive use, the development of chromogenic probes for cyanide detection is of interest for instance in undemanding rapid screening applications. However, chromogenic systems for cyanide in water or in water–organic solvent mixtures are relatively scarce. For instance, cyanide probes have been reported based on the nucleophilic attack of cyanide to blue squaraine derivatives[7] or by the selective reaction of cyanide with subphthalocyanines in aqueous environments.[8] A very recent colorimetric chemosensor has been described involving cyanide complexation to copper(II) from a Cu^{II}–zincon that leaves the zincon ligand free with a colour change.[9] Some other interesting approaches for the detection of cyanide in water include the use of sensor materials. TiO_2 supports functionalised with hemoglobin protein[10] resulted in a highly selective and sensitive detection of CN^- by simply monitoring the changes in the optical properties of the TiO_2 films. The same research group recently attached azophenyl thiourea derivatives onto nanostructured Al_2O_3 films for the selective chromogenic detection of cyanide in water.[11] Organic polymers bearing 2,4,6-triphenylpyrylium moieties have also been used as chromogenic cyanide sensors at pH 11.0.[12] Also remarkable are the examples involving the use of QDs for the detection of cyanide in aqueous environments.[13] In addition to these systems, other examples have been reported for colorimetric signalling of cyanide in organic solvent—water mixtures, usually containing a low percentage of water (frequently lower than 20% by volume).[14]

Receptors **1** and **2** (see Scheme 1) were prepared by electrophilic aromatic substitution between *N*,*N*-dimethylaniline and *N*,*N*-dioctylaniline with 2,6-diphenylpyrylium perchlorate in anhydrous DMF, followed by substitution of the oxygen atom in the pyrylium ring by a sulfur atom in the presence of Na_2S. The ^{1}H-NMR spectra of both receptors were characterized by the presence of the aromatic resonances in the 6.80–8.60 range. The most characteristic signals in this zone are a singlet at *ca.* 8.63 ppm, attributed to the equivalent protons of the thiopyrylium ring, and two doublets centred at 6.90 and 8.20 ppm from the *p*-disubstituted aniline ring.



Scheme 1 The structure of chromoreactands **1** and **2**, and the synthetic procedure for **2**. (i) 1-Bromooctane–K_2CO_3, (ii) 2,6-diphenylpyrylium perchlorate–DMF and (iii) Na_2S–$HClO_4$.

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† Electronic supplementary information (ESI) available: NMR spectra of receptors **1** and **2**. See DOI: 10.1039/b909705h

Fig. 1 Colour changes observed for acetonitrile solutions of chromoreactand **1** (1.0×10^{-4} mol dm^{-3}) in the presence of 10 equiv. of the correspondent anion (except for cyanide; 1 equiv.). From left to right: no anion, Cl^-, Br^-, I^-, NO_3^-, AcO^-, $H_2PO_4^-$, HSO_4^-, NCS^- and CN^-.

Whereas 2,4,6-triphenylthiopyrylium is yellow, 2,4,6-triarylthiopyrylium cations bearing an amine at the *para* position of the 4-aryl group show a deep blue colouration. Thus, acetonitrile solutions of chromoreactands **1** and **2** showed intense absorption in the visible zone centred at *ca.* 575 nm. This visible band most likely has a charge-transfer (CT) character due to the presence of an electron donor aniline group and an electron acceptor thiopyrylium moiety.

In the first step, the colorimetric behaviour of acetonitrile solutions (3.0×10^{-5} mol dm^{-3}) of **1** were tested in the presence of equimolar quantities of certain anions. The addition of 10 equiv. of Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, HSO_4^-, AcO^- and NCS^- to CH_3CN solutions of **1** induced negligible changes in the UV-visible spectra, whereas the addition of 1 equiv. of CN^- anion resulted in complete bleaching (see Fig. 1).

The disappearance of the visible band, instead of a shift, in the presence of cyanide pointed to a chemical reaction between this anion and **1** in a chemodosimeter fashion. Bearing in mind the electrophilic character of the thiopyrylium moiety, we assigned this reaction to an attack of the nucleophile cyanide on the aromatic thiopyrylium ring, which would result in the rupture of the electronic delocalization. The thiopyrylium ring contains one positively charged sulfur atom in its structure, which induces a certain electrophilic character on the C2 and C4 carbons of the heterocycle. In fact, quantum chemical calculations at the semiempirical level indicated that the charge density on atoms C2, C3 and C4 is −0.06, −0.191 and 0.206, respectively.[15] These calculations suggest that the thiopyrylium ring is prone to suffer nucleophilic attack, especially at C4 and to a lesser extent at C2. These calculated charges, together with the fact that the C–S^+ bond in the thiopyrylium ring is somehow polarized by inductive effects, should account for the reactivity observed.

In order to confirm this possible explanation for the observed bleaching, ^{1}H-NMR studies were carried out on mixtures of probe **1** and cyanide in acetonitrile-d_3. The addition of 1 equiv. of CN^- to **1**, results in the formation of a mixture of two different compounds. This can be observed through monitoring the singlet at 8.63 ppm for compound **1**, which turned into three new singlets at 5.96, 6.17 and 7.26 ppm (see Fig. 2). The singlet centred at 6.17 ppm was assigned to the product obtained from nucleophilic attack of the cyanide on C4 of the thiopyrylium ring (structure **I** in Scheme 2), whereas the other two signals were attributed to the product formed by cyanide addition at C2 (structure **II** in Scheme 2). From the areas of the three singlets, a ratio of 75 : 25 for structures **I** : **II** was determined. These results are in agreement with the quantum calculations (*vide ante*).

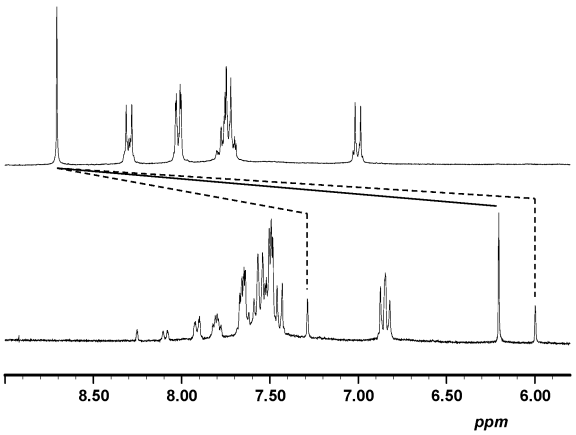
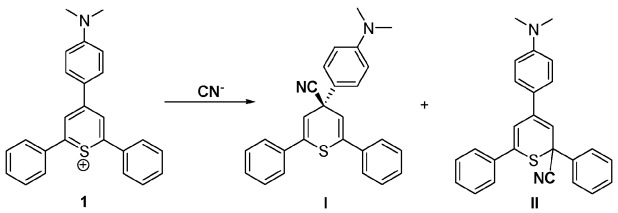


Fig. 2 Top: ^{1}H-NMR spectrum of receptor **1** in CD_3CN showing the aromatic protons. Bottom: ^{1}H-NMR spectrum of receptor **1** in CD_3CN after addition of 1 equiv. of cyanide anion showing the aromatic protons.



Scheme 2 The proposed products obtained from the reaction of CN^- with **1**.

It was also found that the addition of small quantities of water (less than 5%) to acetonitrile solutions of receptor **1** inhibited bleaching in the presence of cyanide. However, we considered that an attractive possibility for overcoming the severe limitation represented by the absence of response of chromoreactand **1** in water could be the use of micelles as nanocontainers, in which **1** and cyanide could find a suitable hydrophobic reaction environment.

The use of functionalized chemosensors embedded in micellar systems for the chromo- and fluorogenic sensing of chemical species in water is a well stabilised field. Very recently, several authors showed that certain binding sites for metal cations and certain fluorophores can be arranged in micelles of surfactants in water, allowing the presence of certain metal cations to be detected by changes in fluorescence.[16] However, to our knowledge, the use of micellar systems for enhanced sensing of anions has only been reported by Anslyn *et al.* for the chromo-fluorogenic recognition of inositol triphosphate in aqueous environments.[17]

With this aim, we prepared receptor **2**, which is similar to **1**, but additionally has its aniline group functionalized with highly hydrophobic *n*-octyl chains in order to facilitate inclusion of the probe into micellar superstructures. As a surfactant, we opted for Triton X-100, which is neutral (average molecular weight of 647 g mol^{-1}), in order to prevent any electrostatic interaction of the surfactant with the charged **2** and cyanide species. In a typical experiment, water solutions were used with a Triton X-100 concentration of 6.47 g L^{-1} (0.01 mol dm^{-3}), which corresponds to an average micelle

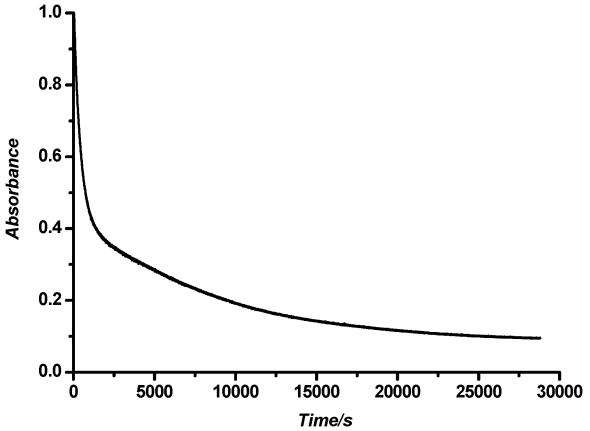


Fig. 3 Changes of the visible band (575 nm) of **2** (1.0×10^{-4} mol dm^{-3} in water at pH 9.5 with 0.01 mol dm^{-3} Triton X-100) in the presence of 10 equiv. of CN^- *vs.* time.

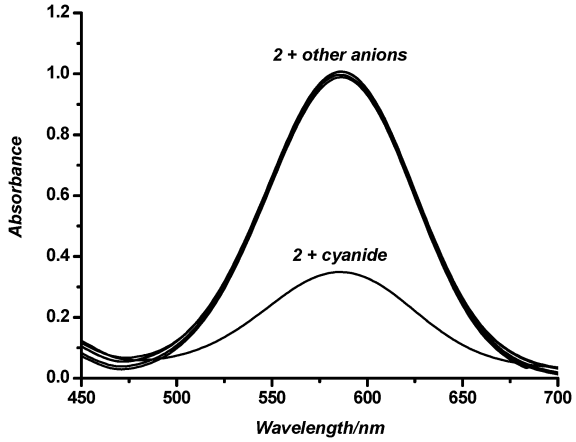


Fig. 4 Changes of the visible band of chromoreactand **2** (1.0×10^{-4} mol dm^{-3} in water at pH 9.5 with 0.01 mol dm^{-3} Triton X-100) in the presence of 10 equiv. of anions F^-, Cl^-, Br^-, I^-, AcO^-, NO_3^-, CN^-, NCS^-, $H_2PO_4^-$, HSO_4^- and CN^-.

concentration of *ca.* 1.0×10^{-4} mol dm^{-3} (for Triton X-100 critical micellar concentration is *ca.* 2.0×10^{-4} mol dm^{-3}, aggregation number 111) and adjusted to pH 9.5. Probe **2** is not soluble in water, but readily dissolves in aqueous solutions containing the surfactant, suggesting the rapid and effective inclusion of **2** into the micelles.

A pH of 9.5 was selected in order to overcome the competition of the OH^- anion in the bleaching mechanism, but at the same time remaining at a pH where the nucleophilic species CN^- can still occur (lower pHs result in the formation of the protonated HCN derivative). In fact, **2** can not be used at very high pH values (higher than 11) because of the rapid and effective nucleophilic attack of the OH^- anion on the thiopyrylium ring. This reaction with OH^-, however, is not effective in aqueous Triton X-100 solutions at pH 9.5, in which **2** remains blue for hours without signs of decomposition.

In the first step we decided to study the kinetic behaviour of chromoreactand **2** (1.0×10^{-4} mol dm^{-3}) adjusted to pH 9.5 in aqueous Triton X-100, in the presence of 10 equiv. of cyanide anion. As can be seen in Fig. 3 only partial bleaching of the solution was observed. However, a remarkable 60% reduction of the intensity of the 575 nm band at 18 min could be observed. This fact is clearly in contrast with the complete bleaching observed in acetonitrile solution and could be ascribed to the energetic barrier imposed by the solvation–desolvation process suffered by cyanide anions in aqueous environments. This solvation process reduces the nucleophilicity of the cyanide anion and, as a consequence, the rate of the reaction with thiopyrylium ring. Fig. 4 shows the visible spectra of chromoreactand **2** (3 mL of micellar aqueous solution 1.0×10^{-4} mol dm^{-3}) before and after addition of 10 equiv. of cyanide anion (visible spectra were recorded after 18 min of cyanide addition). The observed bleaching is consistent with inclusion of the cyanide anion into the micelles and cyanide attack on the thiopyrylium ring. The inclusion of cyanide anions into the micelles excluded the water molecules from the microenvironment of the micellar surface, enabling the chromogenic reaction.

Bearing in mind these favourable characteristics, the reactivity of chromoreactand **2** was tested towards a number of other anions, including F^-, Cl^-, Br^-, I^-, AcO^-, NO_3^-, NCS^-, $H_2PO_4^-$ and HSO_4^- in aqueous Triton X-100 micellar solutions at pH 9.5. In all cases, the presence of these anions resulted in no variation of the band at 575 nm, indicating that the reaction with cyanide is highly selective in water (see Fig. 4). From plots of absorbance at 575 nm *versus* increasing quantities of cyanide added to aqueous micellar solutions of chromoreactand **2** at pH 9.5, a detection limit of *ca.* 1 ppm of cyanide was determined (see Fig. 5).

In conclusion, we have reported the use of anilinium–thiopyrylium scaffolds as probes for the colorimetric detection of cyanide, based on the nucleophilic addition of CN^- to the electron deficient aromatic thiopyrylium ring. Sensitive and selective sensing of cyanide has been obtained by using an undemanding surfactant-assisted protocol. This is one of the very few colorimetric probes described for cyanide detection in pure water. From an alterative viewpoint, the results suggest that surfactants could be a suitable general method of transferring anion-sensing paradigms from the chemistry of organic solvents to the world of colorimetric signalling in aqueous environments.

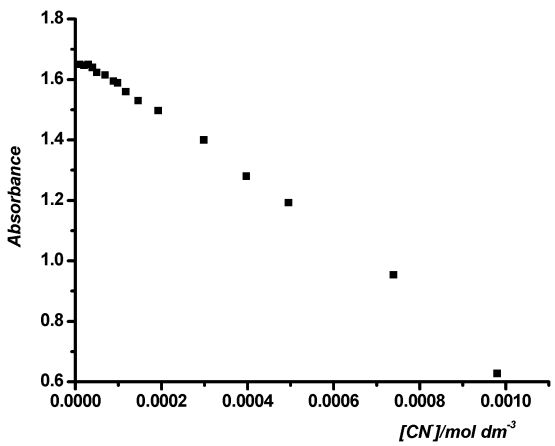


Fig. 5 Changes in the absorbance at 575 nm in micellar solutions of **2** (1.5×10^{-4} mol dm^{-3} in water at pH 9.5 with 0.01 mol dm^{-3} Triton X-100) *vs.* increasing quantities of cyanide anion.

Experimental

Chemicals

Triton X-100, aniline, *N*,*N*-dimethylaniline, 1-bromooctane, triethylorthoformate, acetophenone, sodium sulfide, perchloric acid, potassium carbonate, diethyl ether, acetone, hexane, anhydrous dimethylformamide (DMF) and anhydrous acetonitrile (ACN) were purchased from Aldrich and were used as received. Tetrabutylammonium salts of fluoride, chloride, bromide, iodide, nitrate, dihydrogen phosphate, hydrogen sulfate, acetate, cyanide and isothiocyanate were also purchased from Aldrich and used as received.

Synthesis

All the reactions were carried out with glass material cleaned with nitric acid (in order to avoid contamination from organic matter) and in an inert atmosphere (Ar).

1a: *N*,*N*′-dimethylaniline (0.5 mL, 3.95 mmol) was dissolved in dry DMF (10 mL) and then 2,6-diphenylpyrylium perchlorate (2.63 g, 7.9 mmol) was added. The mixture was heated at 150 °C for 3 h. After this, the mixture was allowed to cool down to room temperature, and then diethyl ether (30 mL) was added and the crude mixture stirred for another 16 h. The final product was isolated by filtration as a dark magenta solid (1.09 g, 2.4 mmol, 61% yield). ^{1}H- and ^{13}C-NMR data, and mass spectra are consistent with those reported in the literature.

1: Pyrylium derivative **1a** (0.36 g, 0.8 mmol) was dissolved in acetone (50 mL) and then Na_2S (2 mL, 10% water solution) was added, and the crude reaction mixture was allowed to react at room temperature for 20 min. Finally perchloric acid (2 mL, 20% water solution) was added and the crude reaction mixture stirred for another 40 min at the same temperature. The final product was isolated by vacuum filtration, and successive washings with water and diethyl ether, as dark blue solid (0.19 g, 0.4 mmol, 50% yield). ^{1}H NMR (300 M Hz, $CDCl_3$): δ = 3.16 (6H, s, N-($C\underline{H}_3$)$_2$), 6.89 (2H, d, $C_6\underline{H}_4$), 7.60 (6H, m, $C_6\underline{H}_5$), 7.88 (4H, m, $C_6\underline{H}_5$), 8.19 (2H, d, $C_6\underline{H}_4$), 8.49 (2H, s, $C_5\underline{H}_2S$). ^{13}C NMR {^{1}H} (75 M Hz, $CDCl_3$): δ = 40.5, 114.3, 122.2, 124.8, 127.7, 130.1, 132.6, 133.2, 134.5, 154.8, 156.6, 160.9. HRMS calc. for $C_{25}H_{22}NS$, 368.1473, found 368.1455.

2a: A mixture of aniline (1.02 g, 11 mmol) and an excess of 1-bromooctane (6.37 g, 33 mmol) was refluxed for 24 h. After cooling, the resulting ammonium salt was washed with NaOH solution, extracted with Et_2O, dried ($MgSO_4$), and evaporated *in vacuo* to give a crude product, which was purified by alumina column chromatography eluting with hexane–diethyl ether 100 : 4. The final product was isolated as white solid (1.58 g, 7.74 mmol, 70% yield). ^{1}H NMR (300 M Hz, acetone-d_6): δ = 0.87 (6H, t, -(CH_2)$_5$-$C\underline{H}_3$), 1.24–1.66 (24, N-CH_2-($C\underline{H}_2$)$_5$-CH_3) 3.07 (4H, t, N-$C\underline{H}_2$), 6.75 (3H, m, $C_6\underline{H}_5$), 7.06 (2H, t, $C_6\underline{H}_5$) ^{13}C NMR {^{1}H} (75 M Hz, acetone-d_6): δ = 14.2, 23.2, 27.8, 30.0, 30.1, 30.3, 32.5, 44.1, 112.9, 116.65, 129.6, 150.0.

2b: Aniline derivative **2a** (0.43 g, 1.2 mmol) was dissolved in dry DMF (10 mL) and then 2,6-diphenylpyrylium perchlorate (0.58 g, 2.4 mmol) was added. The mixture was heated at 150 °C for 3 h. After this, the mixture was allowed to cool down to room temperature, and then diethyl ether (30 mL) was added and the crude mixture stirred for another 16 h. The final product was isolated by filtration as a dark magenta solid (0.42 g, 0.77 mmol, 62.3% yield). ^{1}H NMR (300 M Hz, DMSO): δ = 0.82 (6H, t, -(CH_2)$_5$-$C\underline{H}_3$), 1.19–1.59 (24, N-CH_2-($C\underline{H}_2$)$_5$-CH_3) 3.33 (4H, t, N-$C\underline{H}_2$), 6.88 (2H, d, $C_6\underline{H}_4$), 7.72 (6H, m, $C_6\underline{H}_5$ $C_6\underline{H}_4$), 8.26 (2H, t, $C_6\underline{H}_5$), 8.41 (4H, m, $C_6\underline{H}_5$), 8.59 (2H, s, $C_5\underline{H}_2O$). ^{13}C NMR {^{1}H} (300 M Hz, DMSO): δ = 13.9, 22.1, 26.4, 28.4, 28.7, 29.0, 31.3, 42.4, 109.1, 118.4, 127.5, 129.5, 129.8, 133.4, 135.4, 143.9, 146.9, 156.8, 158.6, 164.7.

2: Pyrylium derivative **2b** (0.42 g, 0.77 mmol) was dissolved in acetone (50 mL) and then Na_2S (0.37 g, 1.5 mmol) in 25 mL of water solution was added, and the crude reaction was allowed to react at room temperature for 20 min. Finally, perchloric acid (1 mL, 20% water solution) was added and the crude reaction mixture stirred for another 40 min at the same temperature. The final product was isolated by vacuum filtration, and successive washings with water and diethyl ether, as dark blue solid (0.23 g, 0.4 mmol, 52% yield). ^{1}H NMR (300 M Hz, CD_3CN): δ = 0.92 (6H, t, -(CH_2)$_5$-$C\underline{H}_3$), 1.32–1.39 (24H, m, N-CH_2-($C\underline{H}_2$)$_5$-CH_3) 3.55 (4H, t, N-$C\underline{H}_2$), 6.97 (2H, d, $C_6\underline{H}_4$), 7.68–7.76 (6H, m, $C_6\underline{H}_5$), 8.00 (4H, d, $C_6\underline{H}_5$), 8.29 (2H, d, $C_6\underline{H}_4$), 8.70 (2H, s, $C_5\underline{H}_2S$). ^{13}C NMR {^{1}H} (300 M Hz, DMSO): δ = 13.5, 22.4, 26.5, 27.3, 28.9, 29.0, 31.5, 51.1, 113.5, 121.7, 125.7, 128.0, 129.9, 132.6, 133.5, 135.2, 154.4, 156.9, 161.0. HRMS calc. for $C_{39}H_{50}NS$, 564.3663, found 564.3660.

Acknowledgements

The authors wish to express their gratitude to the Spanish Government for financial support (projects CTQ2006-15456-C04-01, CTQ2006-15456-C04-02,). T.A. is grateful to the Spanish Government for the fellowship awarded. S.R. would like to thank Generalitat Valenciana for his fellowship.

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