Subphthalocyanines as fluoro-chromogenic probes for anions and their application to the highly selective and sensitive cyanide detection

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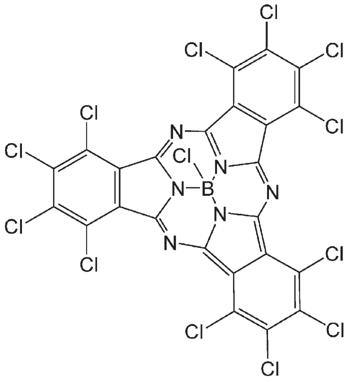
The use of a subphthalocyanine derivative as a selective chromo-fluorogenic reporter for the anion cyanide in mixed aqueous solutions is reported.

There is an increasing attention towards the development of a new generation of chromogenic sensing molecules which have the peculiarity of showing easily observable colour modulations in the presence of target guests.[1] In this respect, anion detection by using chromogenic reagents is an area of emerging interest within the field of anion chemistry. There are not too many examples of chromogenic reagents for anion detection, and a number of them have been reported to work only in organic solvents. However, the search for versatile and tunable highly selective anion probes effective in pure water or water–organic solvent mixtures is still a challenge.[2] Among different approaches to the development of colorimetric sensors those relying on the use of specific anion-induced chromogenic reactions are especially attractive. The goal in this approach takes advantage of the selective reactivity displayed by target anions that generally is accomplished by a highly selective chromo- or fluorimetric response. Following this general interest to anion chemosensing, we report here the use of subphthalocyanines as chemodosimeters for the detection of selected anions. In particular, a selective chromo-fluorogenic detection of cyanide was reached in mixed aqueous solutions to ppm level.

Subphthalocyanines, first synthesized in 1972,[3] are boron-containing macrocycles similar to phthalocyanines but only containing three isoindoline groups.[4] They usually show very interesting optical properties and have found applications in a number of fields.[5] As a suitable representative of this family of compounds, we have selected the derivative **1** (see Scheme 1) that can easily be prepared by reaction of tetrachlorophthalonitrile and boron trichloride following well known procedures.[6] The use of the tetrachloro derivative avoids the formation of several by-products by halogen substitution in the somewhat strong synthetic conditions used.[7] Standard characterization techniques (*i.e.* mass spectroscopy) confirmed the presence of **1**. The absorption and emission spectra of the subphthalocyanine **1** are shown in Fig. 1. **1** shows a typical UV-Vis spectrum in acetonitrile consisting of two intense absorption bands, one at 302 nm (Soret band) and another sharp band at 569 nm (Q band) with a shoulder around 510 nm, possibly associated with vibronic transitions. **1** shows a strong fluorescence emission, even in polar solvents, (*i.e.* in ACN λ_{em} = 581 nm, Φ_F = 0.26, $\tau_{1/2}$ = 3.17 ns) with a weak Stokes shift indicative of a very small distortion of the excited state. Electrochemical studies in acetonitrile were also in agreement with the subphthalocyanine structure with a reversible reduction process at −0.97 V, and an irreversible oxidation at 1.15 V. In addition to its optimal optical properties, the presence of chloride atoms in **1** drastically improves the solubility of this compound in polar solvents when compared with the analogous hydrogen-containing derivative.

As a first step, the chromogenic sensing ability of **1** was studied in acetonitrile in the presence of 100 equivalents of the F^-, Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, HSO_4^-, acetate (Ac^-), CN^- and SCN^- anions. It was clearly observed an elimination of both the Soret and Q bands in the presence of the F^-, $H_2PO_4^-$, Ac^- and CN^- anions. Fig. 2 shows the effect on the spectrum of **1** found upon



Scheme 1 Schematic representation of **1**.

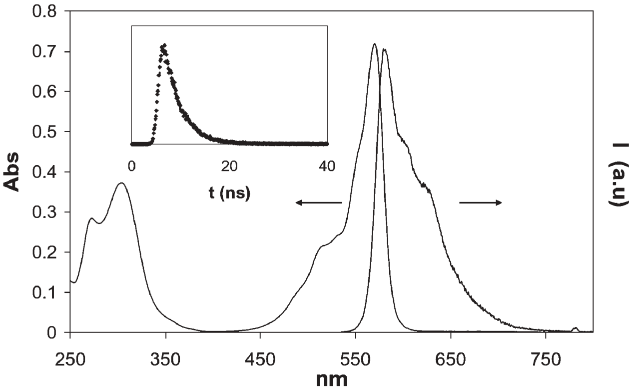


Fig. 1 Absorption ([**1**] = 8.5 × 10^{-6} mol dm^{-3}) and emission spectrum (λ_{ex} = 520 nm) of **1** in acetonitrile. The inset graph shows the fluorescence decay of **1** in acetonitrile.

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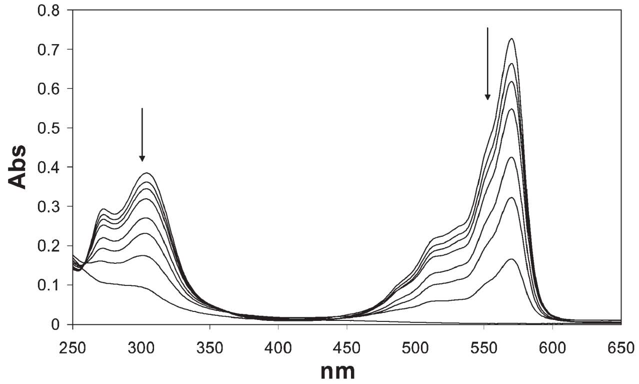

Fig. 2 Changes in the absorption spectrum of **1** (after 5 min) in acetonitrile solution upon increasing cyanide concentrations. ([**1**] = 8.5 × 10^{-6} mol dm^{-3}).

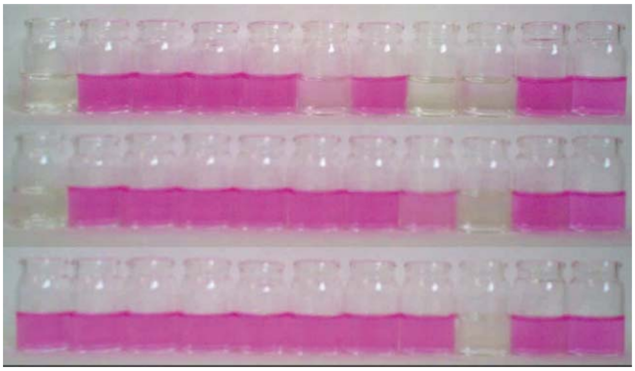

Fig. 3 Colour changes on solutions of **1** ([**1**] = 8.5 × 10^{-6} mol dm^{-3}), in the presence of 100 equivalents of anions, from left to right: F^-, Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, HSO_4^-, Ac^-, CN^-, SCN^-, and no anion. From top to bottom: 0, 1 and 5% vol. water-containing acetonitrile solutions.

the addition of cyanide. Similar graphs were also obtained with the fluoride, dihydrogen phosphate and acetate anions. A photograph of the colour changes induced upon anion addition to acetonitrile solutions of **1** is shown in Fig. 3. A concomitant complete fluorescence quenching in acetonitrile was also observed in the presence of F^-, $H_2PO_4^-$, Ac^- and CN^-.

The bleaching process of solutions of **1** is not instantaneous but increases with time and with the amount of anion equivalents added, strongly suggesting that decoloration is most likely due to an anion-induced chemical reaction. There are mainly three reported modes of reactivity on subphthalocyanines[8] (i) axial reactions with the boron atom, (ii) peripheral reactivity on the aromatic carbons and (iii) ring expansion upon reaction on the imine-type core. Changes in the axial coordination or modifications on the aromatic carbons usually result in quite minor changes in the position of the Soret and Q bands. Therefore the large change in the observed electronic spectrum of **1** must be due to a strong modification on the 14π electron conjugated system as a consequence of an anion attack to the π delocalized polyimine framework. This might additionally be favored by the reversible character of the imine bonds and the geometrically constrained structure of the subphthalocyanine scaffolding. Furthermore, the presence of twelve electron withdrawing chloride atoms in peripheral positions remarkably increases the reactivity towards ring expansion and breaking of the electronic delocalization with the concomitant colour modulation.[9] In fact, whilst this work was being developed a related non-chlorinated subphthalocyanine was reported to react after six hours with fluoride in THF solutions.[10] In a similar fashion, ourselves and others have reported systems in which the attack of nucleophiles to π conjugated systems produced changes in the absorption band.[11]

Despite the interesting reactivity of the subphthalocyanine **1** found in acetonitrile, it shows a rather poor selectivity, since the four anions F^-, $H_2PO_4^-$, Ac^- and CN^- are able to produce a bleaching of the red–pink solutions of **1**. To take advantage of the favourable features of **1** as chemodosimeter but at the same time improve its selectivity we tested the reactivity of **1** in different solvents as a handy method to control anion nucleophilicity and sensing response. Thus, it is known that the nucleophilic character of different species is solvent dependent and that protic solvents decrease the anion's nucleophilicity by hydrogen bonding to the nucleophile's lone pair (solvation effects). A suitable solvent-induced selectivity enhancement was found using water this being a solvent of special concern as it is a suitable media for testing chromo-fluorogenic probes for anions of environmental interest.

The effect of water on the reactivity of **1** with anions is shown in the photographs included in Fig. 3. As stated above, pure acetonitrile solutions of **1** react with the anions F^-, $H_2PO_4^-$, Ac^- and CN^-, but only a 1% vol in water is enough to avoid completely the reaction of **1** with $H_2PO_4^-$ and almost completely with Ac^-. Up to 3% vol of water results in a selective response to fluoride and cyanide anions (not shown), whereas 5% vol water-containing acetonitrile solutions of **1** are remarkably selective to cyanide. In all cases the reaction of **1** with cyanide was found to be relatively fast and typically complete absorbance changes upon cyanide addition were found after 4–5 min. In addition, the plot of the absorbance at 569 nm *versus* cyanide concentration gave typical 1 : 1 binding isotherms from which apparent constants could be calculated (see Table 1). In pure acetonitrile **1** interacts quite strongly with the four anions CN^-, F^-, Ac^- and $H_2PO_4^-$. However, upon addition of small amounts of water the apparent constants for fluoride, acetate and dihydrogen phosphate are drastically reduced (*i.e* from *ca.* 1 × 10^5 to <100 for fluoride), whereas that for cyanide remains relatively high (*i.e* from 4 × 10^5 to 1 × 10^4). Data in Table 1 is in agreement with the photographs shown in Fig. 1.

This selective response to cyanide is an interesting result as cyanide is a highly toxic anion 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. Yet, there are relatively few examples of colorimetric probes for cyanide[12] compared with the number of chromogenic chemosensors for certain anions such as fluoride or carboxylates.[13] However, due to its wide use and its serious toxicity the development of new chromo-fluorogenic chemosensors for cyanide in water or mixed aqueous solutions can be of interest,[14] *i.e.* for rapid undemanding screening applications. In this field, chromogenic optical probes may play a primary role. In this respect, interesting recent examples on fluorescence cyanide detection have been reported based on the selective complexation of cyanide with boronic acid derivatives.[15]

Table 1 Apparent binding constants of **1** with cyanide in pure acetonitrile and in the presence of 1, 3 and 5% of water

% H_2O^a	CN^-	F^-	Ac^-	$H_2PO_4^-$
0	$(4.4 \pm 0.5) \times 10^5$	$(1.3 \pm 0.2) \times 10^5$	$(6.6 \pm 0.6) \times 10^5$	$(6.9 \pm 0.9) \times 10^3$
1	$(2.2 \pm 0.1) \times 10^5$	$(2.6 \pm 0.2) \times 10^4$	$(5.6 \pm 0.2) \times 10^3$	<100
3	$(3.5 \pm 0.4) \times 10^4$	$(6.3 \pm 0.5) \times 10^2$	<100	<100
5	$(1.2 \pm 0.1) \times 10^4$	<100	<100	<100

[a] % of water in acetonitrile : water mixtures (*v* : *v*).

Stimulated by the favourable features of the response of **1**, we took a step further and tested the potential determination of cyanide in acetonitrile : water mixtures. The performance of **1** as a chromo-fluorogenic probe was thus tested in buffered mixed aqueous solutions (acetonitrile : water 1 : 1) at pH 7 (HEPES, 0.01 M) and pH 9.6 (CHES, 0.01 M) in the presence of a number of anions. At both pHs cyanide induced a clear selective bleaching of the red–pink solutions of **1** but the solution buffered with CHES displayed a higher sensitivity. This latter effect is somewhat expected and due to a shift, at basic pH, of the acid–base HCN/CN^- equilibrium in water towards the nucleophilic CN^- anion. At pH = 9.4 amounts of cyanide as low as 0.1 ppm were able to produce significant spectrophotometric changes on **1**, whereas the detection limit at pH 7 was about 10 ppm of cyanide. Although this low detection limit might be enough for cyanide detection, for instance in drinking water, even lower detection limits could be afforded through fluorescent techniques due to the relatively high quantum yield displayed by subphthalocyanines ($\Phi_F = 0.25$ for **1** in acetonitrile : water 1 : 1 mixtures).

In summary, we have reported the use of subphthalocyanines as probes for the detection of selected anions. In particular, a selective chromo-fluorogenic detection of cyanide was reached in mixed aqueous solutions to the ppm level due to the selective reaction of this anion with a selected subphthalocyanine. The method is easy and allows selective detection "by the naked eye" of very low cyanide concentrations.

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