



Anionic chromogenic chemosensors highly selective for cyanide based on the interaction of phenyl boronic acid and solvatochromic dyes



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ABSTRACT

Solutions of two solvatochromic dyes, Reichardt's pyridinium *N*-phenolate betaine (**1**) and Brooker's merocyanine (**2**), are colored in acetonitrile but become colorless when phenyl boronic acid (**PBA**) is added due to the formation of covalently linked dye-**PBA** species. Of the various anions added, only F⁻ and CN⁻ caused the reappearance of the original color related to the free dye in solution. These anions act as nucleophiles in acetonitrile and displace the dye leaving group. On the addition of very small amounts of water the system becomes highly selective toward CN⁻ because of the ability of water to strongly solvate F⁻, inhibiting its nucleophilic action, while CN⁻ is sufficiently naked to react with dye-**PBA** species. The titrations of the dye-**PBA** complexes with CN⁻ revealed that the shape of the curves is dependent on the experimental conditions. With the use of large amounts of **PBA**, the dye, after being displaced, interacts with the free **PBA** forming hydrogen-bonded complexes, which are disrupted with the addition of an excess of the anion. This was not observed in aqueous acetonitrile since water can form hydrogen bonds with the boronic acid and with the dye, preventing the formation of dye-**PBA** hydrogen-bonded complexes.

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1. Introduction

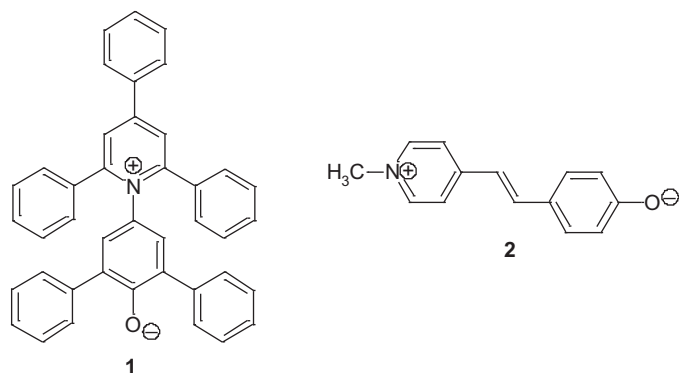
The development of different strategies for obtaining optical chemosensors for anionic detection is an important challenge which many research groups have confronted in recent years [1–13], due to the fact that anionic species play a very important role in many chemical and biological processes. In this regard, many optical chemosensors have been developed for fluoride (F⁻) [14–16] and cyanide (CN⁻) [17]. F⁻ is an essential trace element which plays an important role in industrial processes, environmental pollution, the development of many diseases, and the prevention of dental caries and osteoporosis [18–20]. CN⁻ has many applications in the metallurgy, fishing, mining, and in the fabrication of polymers [21–23]. Also, its monitoring in some fruit seeds and roots that release CN⁻ through hydrolysis is an important issue [24]. Another important source of undesired CN⁻ ions in the atmosphere is toxic smoke due to fire. Methods are required for both easy environmental detection and the monitoring of blood levels

due to exposure during life-saving treatments. The most challenging concern in relation to blood monitoring is the short half-life and the poor stability of CN⁻ [25]. This anion is lethal in very small amounts due to its ability to bind strongly to the active site of cytochrome-oxidase, which leads to the inhibition of the mitochondrial electron transport chain and consequently to a decrease in the oxidative metabolism [21–23]. Many chemical warfare compounds, such as sarin, soman, and tabun [26–28] deliver F⁻ and CN⁻ through hydrolysis [29] and this has motivated the development of efficient optical chemosensors able to detect these neurotoxic agents [30–33].

Our research group has developed chromogenic chemosensors for F⁻ and CN⁻ based on solvatochromic compounds having a phenolate moiety in their molecular structure [34–38], such as Reichardt's pyridinium *N*-phenolate betaine dye, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (**1**), and 1-methyl-4-[(1-oxocyclohexa-2,5-dienylidene)ethylidene]-1,4-dihydropyridine, known as Brooker's merocyanine (**2**), which have been commonly used as perichromic probes in the investigation of the polarity of different media [39–43]. Another component of the chemosensor set is comprised of boronic acids which are used in supramolecular devices as efficient recognition units,

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Scheme 1. Molecular structures of the merocyanines **1** and **2**.

especially for monosaccharides and anionic species, such as F^- and CN^- [15,44–49]. Therefore, a displacement strategy involving compound **2** and phenyl boronic acid (**PBA**) was studied for the development of a chromogenic chemosensor which is highly selective toward F^- among other anionic species [35]. Compound **2** in acetonitrile is colored, but it reacts with **PBA** forming a **2-PBA** intermediate which is colorless in solution. With the addition of F^- to the medium the original color of the solution is restored because the anion reacts with the boron center displacing **2** [35]. In other related study, Cha et al. developed a chromogenic chemosensor for F^- based on a displacement assay using a merocyanine as the signaling unit and **PBA** [50]. Although boronic acids have been utilized as recognition units in optical chemosensors for the detection of CN^- [48,49,51–53], this anion was not studied in the previous reports that make use of **PBA**-merocyanine displacement assays.

In this paper, compounds **1** and **2** (Scheme 1) and **PBA** were used to study an anionic chromogenic chemosensor based on the displacement of the dye from the boron center caused by the nucleophilic attack of the anion on the boron center of the intermediate. The data obtained show that this system can be used to detect F^- and CN^- in acetonitrile, being highly selective toward CN^- over F^- when very small amounts of water are added to the medium. In addition, the experimental evidence obtained allowed the proposal of a model to describe this system as an anionic chromogenic chemosensor.

2. Experimental

2.1. Materials

All chemicals used were high-purity commercial reagents. The deionized water used in the measurements was boiled and bubbled with nitrogen and kept in a nitrogen atmosphere to avoid the presence of carbon dioxide. Acetonitrile (HPLC grade, Sigma–Aldrich) was dried with calcium hydride, distilled and stored over molecular sieves (Sigma–Aldrich 4 Å) as previously described [54]. Karl-Fischer titrations were performed with this solvent and demonstrated the presence of water in a concentration of $7.1 \times 10^{-3} \text{ mol dm}^{-3}$ (0.016%). Tetra-*n*-butylammonium hydroxide was purchased from Sigma–Aldrich. All anions (HSO_4^- , $H_2PO_4^-$, NO_3^- , CN^- , CH_3COO^- , F^- , Cl^- , Br^- , and I^-) were used as tetra-*n*-butylammonium salts with purity greater than 97–99%. The anions were purchased from Fluka (F^- , >97%; Cl^- , >98%; NO_3^- , >97%; $H_2PO_4^-$, >97%), Vetec (Br^- , >99%; I^- , >99%; HSO_4^- , >99%), and Sigma–Aldrich (CH_3COO^- , >97%) and were dried over phosphorous pentoxide under vacuum before use. Karl-Fischer experiments were performed for the following tetra-*n*-butylammonium salts in order to determine the content of water

in each salt: CN^- (0.12% water), F^- (1.13% water), $H_2PO_4^-$ (0.11% water), and CH_3COO^- (0.07% water). CuI (98%) was purchased from Sigma–Aldrich. Buffered water using HCl/Tris (2-amino-2-hydroxymethyl-propane-1,3-diol; pH = 8.99) as the buffer was used in these experiments and in the titrations. This solution was prepared using hydrochloric acid solution in a concentration of $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ and Tris was added to form a buffered medium with the pH required. Dye **1** was synthesized according to a method described in the literature [55], recrystallized three times from hot water and dried under vacuum. Compound **2** was synthesized as described previously [41].

2.2. General methods

UV–vis absorption spectra were obtained with a Varian (Cary Bio 50) or HP 8452A spectrophotometer, equipped with a thermostated bath, employing a 1 cm quartz cuvette. The maximum wavelengths (λ_{max}) on the UV–vis spectra were calculated from the first derivative of the absorption spectrum. The titration experiments were performed using a microsyringe and were carried out using flasks and cuvettes hermetically closed with rubber stoppers in order to minimize evaporation.

2.3. Naked-eye detection and UV–vis spectra

Firstly, a solution of the dye (50 cm^3) was prepared in acetonitrile at concentrations of 2.0×10^{-4} and $2.0 \times 10^{-5} \text{ mol dm}^{-3}$ for dyes **1** and **2**, respectively. **PBA** was added to this solution to form the dye-**PBA** system, with **PBA** concentrations of $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ for dye **1** (**PBA/1** mole ratio of 15) and $c(\text{PBA}) = 5.6 \times 10^{-4} \text{ mol dm}^{-3}$ for dye **2** (**PBA/2** mole ratio of 28). The resultant colorless solutions were used to prepare stock solutions (2.0 cm^3) of the anions (CN^- , F^- , Cl^- , Br^- , I^- , $H_2PO_4^-$, HSO_4^- , and NO_3^-) at concentrations of $1.8 \times 10^{-3} \text{ mol dm}^{-3}$. Subsequently, more diluted anion solutions ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$ and $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ for systems with dye **1** and **2**, respectively) were prepared using glass vials, photographs were taken, and the UV–vis spectra were obtained. Small amounts of buffered water (HCl/Tris, pH = 8.99) were added to each vial and again photographs and UV–vis spectra were obtained.

The assay for the stoichiometry determination was performed in acetonitrile with the method of continuous variations (Job's method). This plot was obtained considering the formation of **1-PBA** produced from dye **1** and **PBA**. This study was performed at 25.0°C using stock solutions with concentrations of $4.0 \times 10^{-4} \text{ mol dm}^{-3}$ for **1** and $6.0 \times 10^{-4} \text{ mol dm}^{-3}$ for **PBA** and the absorbance values were read at $\lambda_{max} = 622 \text{ nm}$.

The experiment to verify the reversibility of the studied system was performed as follows. Firstly, a solution of compound **1** was prepared in acetonitrile in the presence of 1.1% water at a concentration of $1.7 \times 10^{-4} \text{ mol dm}^{-3}$. **PBA** was added to this solution to form the **1-PBA** system, with **PBA** concentrations of $1.7 \times 10^{-3} \text{ mol dm}^{-3}$. The resultant colorless solutions were used to prepare a solution (2.0 cm^3) of CN^- , at a concentration of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$, to which CuI was added, with $c(CuI) = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$.

2.4. Titration studies

2.4.1. Titration of compound **1** with **PBA**

A solution in acetonitrile of dye **1** ($2.0 \times 10^{-4} \text{ mol dm}^{-3}$) was prepared and used to make up a solution of **PBA** ($4.1 \times 10^{-3} \text{ mol dm}^{-3}$). Subsequently, 1.5 cm^3 of the dye solution was placed into a quartz cuvette closed with a rubber septum. After being thermostated at 25.0°C , the UV–vis spectrum was recorded. Small volumes of **PBA** solution were added to the cuvette, using a microsyringe,

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