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An anionic chromogenic sensor based on protonated Reichardt's pyridiniophenolate

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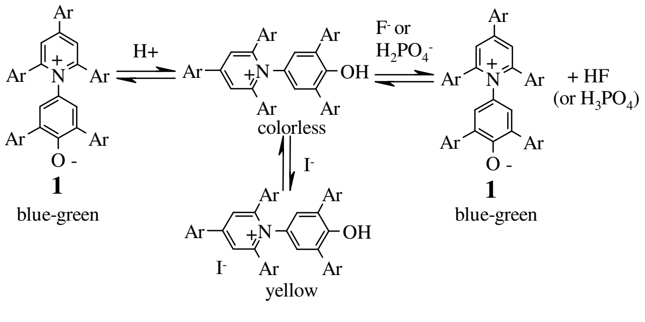
Abstract—An anionic sensor based on Reichardt's betaine is described here. The dye is blue-green in chloroform but becomes colorless under protonation. Increasing amounts of different anions were added into the solution of the protonated dye. The addition of F^- and $H_2PO_4^-$ caused the reappearance of the original blue-green color, while the addition of I^- made the solution of the protonated dye yellow. The observations are discussed based on the fact that F^- and $H_2PO_4^-$ can act as bases accepting a proton from the protonated dye and also in relation to the formation of a complex between the protonated dye and iodide.

The recognition and the detection of anionic species is a field of increasing interest due to the fact that anions play a fundamental role in many chemical and biological processes.[1] Much effort is being spent in the development of sensors not only to perform selective anion detection visually, but which also allow the quantification of such species.[2–5] Although the literature reports many examples of fluorescence anion sensors,[2,4] in comparison, the development of simple and common colorimetric sensors for anionic species is still limited.[3–5]

Merocyanine dyes are heterocyclic compounds with many applications.[6] Reichardt's betaine, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (**1**), is a very well-known example of these dyes.[7] Considerable work has been devoted to this compound since its discovery nearly four decades ago,[8] due to its solvatochromism (its UV–vis spectrum changes if the polarity is altered).[7] The maximum absorption of **1** in different solvents represents the basis for the Reichardt polarity parameter $E_T(30)$[7] and this dye has been extensively used as a probe, for instance in the study of mixed solvents,[9] microheterogeneity in solution,[10] kinetics,[11] ionic liquids,[12] and solutions containing cyclodextrins.[13] Although this dye has also been used in the investigation of salt solutions,[14] it is well known that it can be used to detect only cationic species, mainly due to the interaction of the cation with the negatively charged phenolate moiety.[14] Thus, the UV–vis spectrum of dye **1** does not undergo alterations following the addition of anionic species.

Recently, Hong and co-workers reported a fluoride-selective chromogenic sensor based on the fact that azophenols can interact with anions through hydrogen bonding and on the basicity of the anions.[15] Here, we wish to show that it is possible to 'teach a new trick to the old dye': its protonation allows it to act as an anionic sensor, as shown in Scheme 1. Compound **1** was initially solubilized in chloroform which contained traces of water and protonated by H_2CO_3 generated by bubbling CO_2 through it.[16] The protonation made the blue-green solution of **1** colorless. Increasing amounts of different



Scheme 1.

Keywords: Anionic sensor; Fluoride; Pyridiniophenolate; Chromogenic sensor.

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anions (F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, and NO_3^-) were then added to the colorless solution of the protonated dye.[17] It was found that only the addition of F^- and $H_2PO_4^-$ caused the reappearance of the original blue-green color (Fig. 1). Interestingly, the addition of I^- turns the solution of protonated **1** yellow, which allows the visual discrimination of the studied anions.

UV–vis spectra were taken of **1** and of the protonated dye in chloroform after the addition of each anion. It can be observed that a solution of dye **1** displays a solvatochromic band at 731 nm, which is in agreement with the literature.[7] It is well known that the addition of hydroxylic species to dye **1** in chloroform causes a hypsochromic shift in its solvatochromic band due to the formation of a hydrogen bond between the phenolate donor moiety in the probe and the OH group from the species added.[13,18] The addition of F^- and $H_2PO_4^-$ anions to protonated **1** leads to reappearance of the solvatochromic band. The similar wavelength behavior of deprotonated **1** and protonated **1** in the presence of the anions does not reflect the formation of hydrogen-bonded anion: protonated **1** complexes, but rather indicates that these anions are able to act as bases, accepting protons donated by the protonated dye and generating **1** in solution. The slight hypsochromic shift observed on comparing the position of the solvatochromic band of **1** with that of the same band of **1** in the presence of the anions is due to a halochromic behavior caused by the increase in the medium polarity with the addition of the salts.[14]

Titration experiments were performed to quantify the influence of the increase in the anion concentrations on the solutions of the protonated pyridiniophenolate. The sequence of UV–vis spectra shown in Figure 2 for a titration with fluoride is similar to that obtained for dihydrogenphosphate (not shown): the addition of the anion leads to the appearance of the solvatochromic band at 728 nm. A plot of the absorbance values at 728 nm as a function of the concentration of fluoride displayed a linear behavior until the dye and fluoride concentrations were the same (Fig. 3). This provides an important evidence for an equilibrium strongly shifted toward the formation of HF with the participation of the dye and the anion in a 1:1 stoichiometry. A fitting of the experimental data[19,20] gave a binding constant of $(7.08 \pm 4.03) \times 10^7$ dm^3 mol^{-1}.

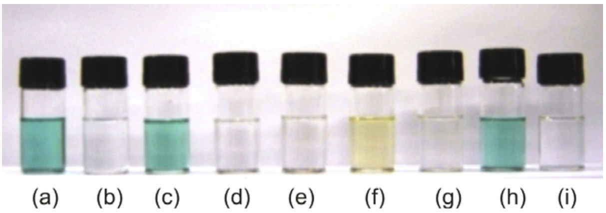

Figure 1. Chloroform solutions of (a) dye **1**, (b) protonated **1** (both 1.7×10^{-5} mol dm^{-3}), and protonated **1** in the presence of (c) F^-, (d) Cl^-, (e) Br^-, (f) I^-, (g) NO_3^-, (h) $H_2PO_4^-$, and (i) HSO_4^- as tetrabutylammonium salts at a concentration of 1.0×10^{-3} mol dm^{-3}.

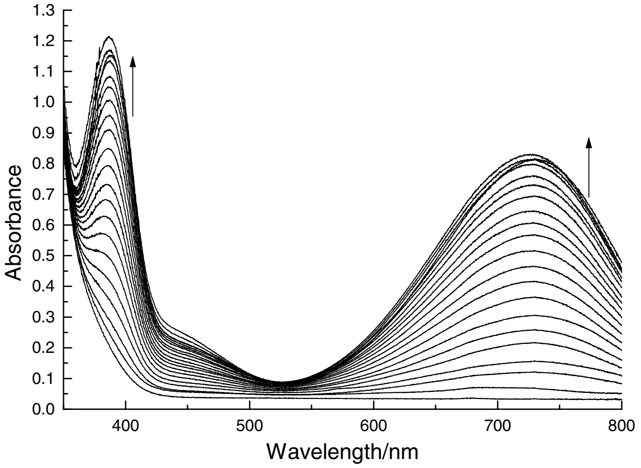

Figure 2. UV–vis spectra of protonated **1** (1.7×10^{-5} mol dm^{-3}) in chloroform at 25 °C after the addition of increasing amounts of tetrabutylammonium fluoride anion. The final concentration of F^- was 6.7×10^{-4} mol dm^{-3}.

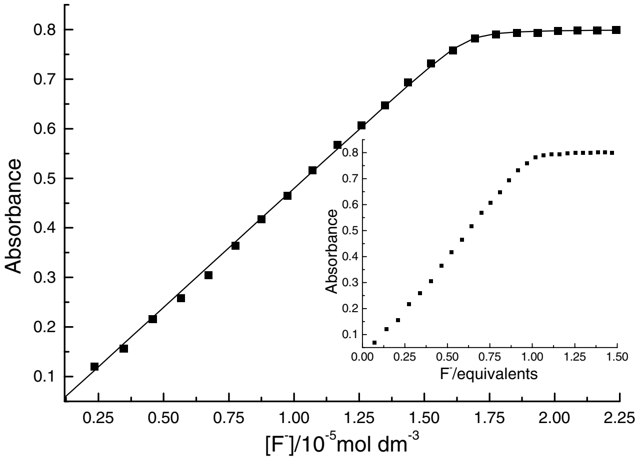

Figure 3. Variation in the absorbance at 728 nm of protonated dye **1** in chloroform with the addition of increasing amounts of tetrabutylammonium fluoride. The experiment was performed at 25 °C and the concentration of **1** was 1.7×10^{-5} mol dm^{-3}.[19] The inset displays a mole ratio plot for the interaction of protonated **1** with fluoride, which clearly indicates a 1:1 stoichiometry.

Figure 4 shows a plot of absorbance values as a function of dihydrogenphosphate added. From this plot a binding constant of $(5.61 \pm 0.14) \times 10^4$ dm^3 mol^{-1} is obtained.[19] The results obtained suggest that fluoride is a stronger base than dihydrogenphosphate in chloroform which helps to explain the observed selectivity in relation to the anions studied. It is important to observe that the greater effect of fluoride is related to its smaller size, higher charge density, and higher electron affinity, important properties which make it capable of forming a stronger interaction with the phenol group in **1**. These aspects have been pointed by other authors in order to explain the very high selectivity to fluoride in comparison to other anions of phenol-based chromo and fluorogenic sensors.[15,21–23] Recently, Wang and co-workers showed that conjugated polymers with phenol unities in their structures can act as fluorescent and colorimetric

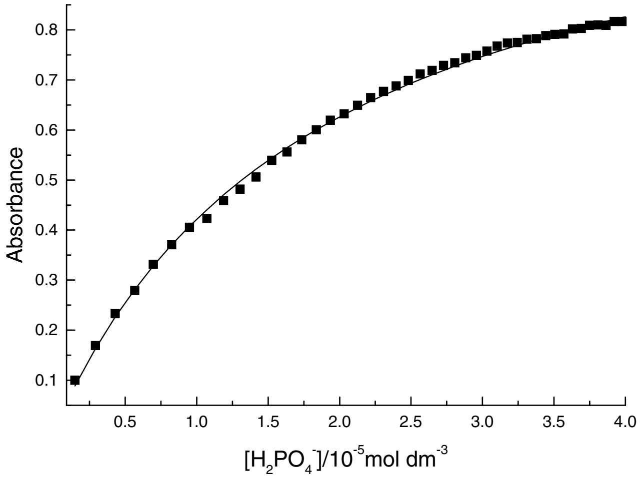

Figure 4. Variation in the absorbance at 728 nm of protonated dye **1** in chloroform with the addition of increasing amounts of tetrabutylammonium dihydrogenphosphate.[19] The experiment was performed at 25 °C and the concentration of **1** was 1.7×10^{-5} mol dm^{-3}.

sensors in chloroform.[23] In addition, as in our work, they verified that the chemosensors are highly sensitive to fluoride in relation to other anions and a low sensitivity was also observed for dihydrogenphosphate, while other anions did not cause alterations in the fluorescence or absorption spectra of the sensors in solution.[23] In another related study, Piatek and Jurczak reported an anionic chromogenic sensor able to differentiate selectively between fluoride and dihydrogenphosphate.[24] Although in these studies evidence for the formation of hydrogen-bonded complexes formed between the sensors and anions is presented,[15,21–24,26] the evidence provided here comprises the complete proton transfer from the protonated dye to the anion.

Titration experiments were also performed through the addition of increasing amounts of iodide to a solution of the protonated dye (Fig. 5). It was found that the addition of iodide led to the appearance of a new band at 381 nm. It is well known that *N*-alkyl pyridinium cations can form charge-transfer complexes with iodide in solution.[25] Thus, pyridiniophenolate **1**, once protonated on its phenolate donor moiety, loses its characteristic charge-transfer transition in the visible region,[7] but the acceptor pyridinium group can still form a complex with iodide, which has a charge-transfer feature. An association constant in chloroform, of $(2.11 \pm 0.07) \times 10^5$ dm^3 mol^{-1},[19] was calculated from the data.

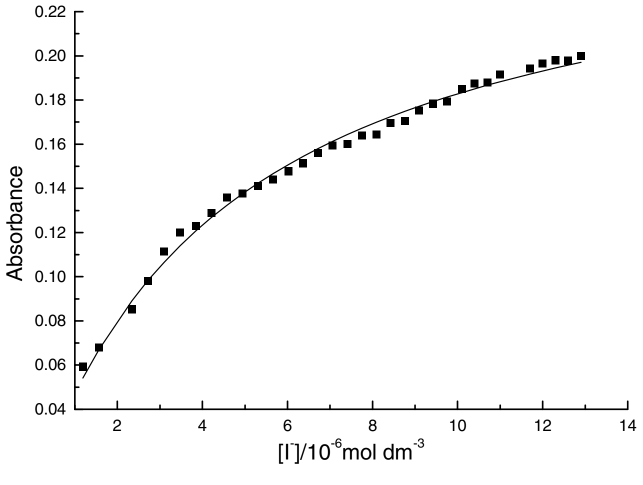

Figure 5. Variation in the absorbance at 381 nm of protonated dye **1** in chloroform with the addition of increasing amounts of tetrabutylammonium iodide.[19] The experiment was performed at 25 °C and the concentration of **1** was 1.7×10^{-5} mol dm^{-3}.

In summary, it is shown here that the classical pyridiniophenolate **1** is able, after protonation, to act as an anionic chromogenic sensor which works due to two different features: acidity/basicity and complexation leading to an intermolecular charge-transfer nature. An aspect common to this study and other recent studies[15,21–24,26] is the design of chemosensors with an acidic site for recognizing more basic anions. Since many structural modifications to dye **1** and related merocyanines can be carried out,[6–8,12] a change in the acidity of these dyes would be expected to make these chromo and fluorogenic sensors more efficient.

Acknowledgements

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16. Karl–Fischer measurements revealed that the chloroform employed contained water in a concentration of $3.56 \times 10^{-3}\,\text{mol dm}^{-3}$, which was sufficient to interact with the CO_2 and, consequently, to acidify the medium.
17. The experiments were performed as follows: a stock solution of **1** ($1.7 \times 10^{-5}\,\text{mol dm}^{-3}$) was prepared in anhydrous chloroform. After that, CO_2 was bubbled into this solution with a syringe in order to protonate the dye. This colorless solution was then used to prepare the stock solution of the anion. Titration experiments were performed by adding small amounts of this solution with a microsyringe to closed quartz cuvettes containing the solution of protonated **1**. These solution transfer experiments were carried out using flasks and the cuvettes were hermetically closed with rubber stoppers in order to minimize problems with the evaporation of the chloroform and all experiments were carried out at 25 °C.
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19. Data related to the fluoride experiments were fitted with the use of the following equation:[20] $\text{Abs} = \text{Abs}_0 + (\text{Abs}_{\max} - \text{Abs}_0)/2C_1 \quad \{C_1 + C_{A-} + 1/K - [(C_1 + C_{A-} + 1/K)^2 - 4C_1C_{A-}]^{1/2}\}$, while the experiments with dihydrogenphosphate and iodide were fitted by means of the equation $\text{Abs} = (\text{Abs}_0 + \text{Abs}_{\max}\ KC_{A-})/(1 + KC_{A-})$.[20] In these equations, Abs is the absorbance value after each addition of the anion, Abs_0 is the initial absorbance without anion added, $\text{Abs}_{\max}$ is the maximal absorbance value obtained by the addition of the anion, C_1 is the concentration of **1**, C_{A-} is the concentration of the anion in each addition and K is the binding constant. The values of χ^2 for the plots were 5×10^{-5} (F^-), 7×10^{-5} ($H_2PO_4{}^-$), and 1×10^{-5} (I^-). A discussion on the use of these equations, as well their deductions, can be found in Ref. 20.
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