# A Molecular Colour Sensor for Fluoride

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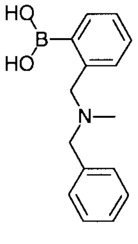
An azo dye molecule with a boronic acid receptor unit has been used to create a fluoride selective colour sensor.

The design and synthesis of anion molecular receptors is the focus of many research groups. Anion receptors can consist of protonated nitrogens, metal ions, hydrogen bonding sites and Lewis acid receptors.[1–7] There is interest in following the uptake and metabolism of fluoride in both plants and animals and in the analysis of drinking water.

Fluoride concentrations are currently determined using electrodes prepared from lanthanum fluoride.[8] Colorimetric assays for fluoride have also been well documented.[9–11] However, the colorimetric detection of anions such as fluoride using designed receptors is a more recent development.[12–16]

The system presented here is of the designed receptor type and is based on the Lewis acid–base interaction between boron and anions. When boron binds with certain anions the hybridisation changes from $sp^2$ to $sp^3$.[17,18] Shinkai has recently developed a fluoride receptor based on ferrocene boronic acids, the binding is measured electrochemically[19] or by the colour change of a redox coupled dye molecule.[20]

We previously reported a fluorescent system for the recognition of fluoride ions in water (compound **1**).[21] The intramolecular hydrogen bond formed between the protonated amine of compound **1** and fluoride stabilises the monofluoride adduct.[21] In contrast simple commercial aromatic boronic acids form trifluoride adducts.[21,22]



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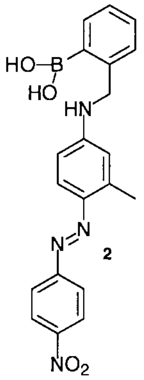

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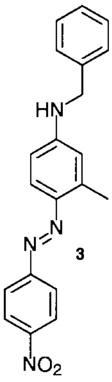

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With this research we set out to extend our previous work and develop molecular receptors for fluoride, which produce a visible colour change. For this investigation we used azo dye molecule **2**[23] and model azo dye compound **3.**[24]

When azo dye molecule **2** is titrated with potassium chloride, bromide and iodide, the orange absorbance at 450 nm increases in intensity. Also when model compound **3,** with no boronic acid binding site, is titrated with potassium fluoride, the orange absorbance at 468 nm increases in intensity. The increase in the intensity of absorbance at 450 nm and 468 nm for azo dye molecules **2** and **3** with added potassium halides is attributed to an increase in the dielectric constant of the solution. It is well documented that changes in solvent polarity can affect the intensity of absorbance of azo dye molecules.[25]

When azo dye molecule **2** is titrated with potassium fluoride in methanol the colour changes from orange (450 nm) to claret (563 nm). The spectral changes associated with this titration are shown in Figure 1.

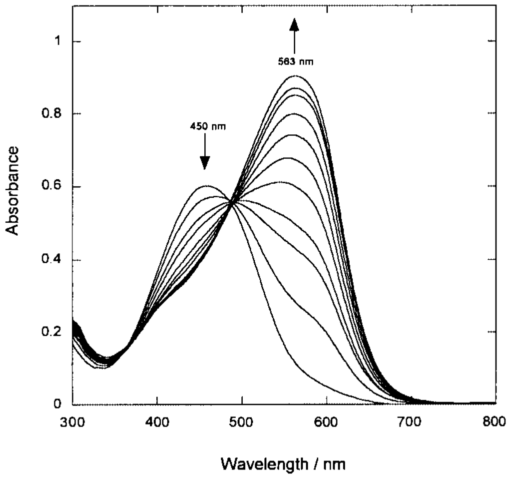
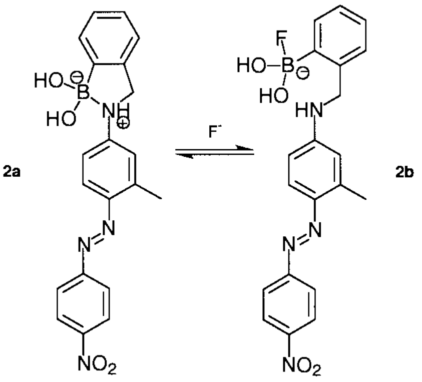


**Figure 1**. Absorption spectral changes of dye molecule **2** ($3.16\times10^{-5}$ mol $dm^{-3}$) with increasing concentration of KF in MeOH. The curves illustrated are for the following [KF]; 0, $9.98\times10^{-4}$, $2.32\times10^{-3}$, $3.99\times10^{-3}$, $5.85\times10^{-3}$, $7.75\times10^{-3}$, $9.07\times10^{-3}$, $1.08\times10^{-2}$, $1.30\times10^{-2}$, $1.51\times10^{-2}$, $1.67\times10^{-2}$ mol $dm^{-3}$.

The observed colour changes, if any, induced upon addition of potassium halides to azo dye molecule **2** are shown in Figure 2.

**Figure 2.** Colour of **2** ($3.48\times10^{-5}$ mol $dm^{-3}$) in MeOH with and without 0.01 mol $dm^{-3}$ KX. From left to right: **2**; **2** with KF; **2** with KCl; **2** with KBr; **2** with KI.

The colour of **2** changes from orange to claret on addition of potassium fluoride. This is a similar colour change to that observed for the pH titration of **2**.[23] The colour change with pH is associated with the formation of a tetrahedral boronate anion. Therefore, the addition of potassium fluoride to a solution of azo dye molecule **2** in methanol must also be producing a tetrahedral boronate anion. Formation of a boronate anion can only be achieved if the B–N bond of orange coloured species **2a** is broken to give the claret coloured species **2b** (Scheme 1).



**Scheme 1.**

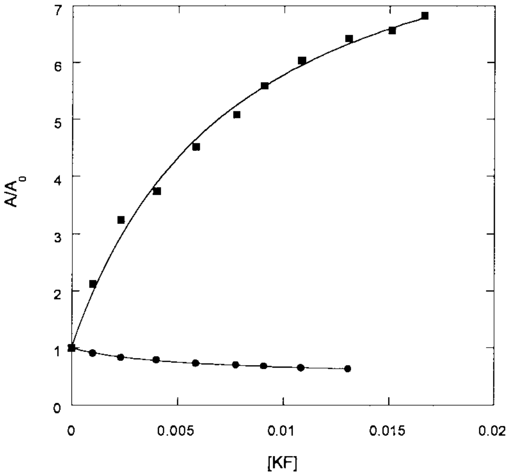


**Figure 3.** Relative absorbance *versus* [KF] profile of azo dye molecule **2** ($3.16\times10^{-5}$ mol dm$^{-3}$), (■) 563 nm and (●) 450 nm in MeOH.

The normalised absorbance at 450 nm and 563 nm versus concentration profiles are shown in Figure 3. The experimental curves are fitted assuming the formation of a monofluoride adduct.[26] The result is reasonable since only the fluoride ion which breaks the B–N bond will be observed spectroscopically. The fluoride stability constants $K$ determined from the best fit of these curves are 130 ± 10 dm$^3$mol$^{-1}$ (563 nm) and 190 ± 20 dm$^3$mol$^{-1}$ (450 nm). Since this system must be experiencing a similar solvent polarity affect as outlined above, the true stability constant should lie between these two values. These two values are also comparable with the previously determined stability constant $K$ for compound **1** of 101 dm$^3$mol$^{-1}$.[21]

The use of this simple azo dye molecule has resulted in high fluoride selectivity. We believe that with appropriate modifications of the molecular receptor, fluoride selectivity can be fine-tuned to any desired fluoride concentration range. It is hoped that this work will lead to the development of fluoride colour sensors for a variety of industrial and medicinal applications.

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24 Selected data for **3**: mp 147–149 °C (decomp.); (Found: C, 69.10; H, 5.43; N, 6.25%. Calcd for $C_{20}H_{18}N_4O_2$: C, 69.35; H 5.24; N 6.17%); $\nu_{max}$(KBr)/cm$^{-1}$ 1604s, 1507s, 1328s; $\delta_H$ (300.1 MHz; $CDCl_3$; $Me_4Si$) 2.67 (3 H, m), 4.43 (2 H, d, $J$ 6.0 Hz), 4.71 (1 H, t, $J$ 6.0 Hz), 6.47–6.55 (2 H, m), 7.25–7.38 (5 H, m), 7.73–7.78 (1 H, m), 7.86–7.92 (2 H, m), 8.27–8.33 (2 H, m); $\delta_C$ (75.5 MHz; $CDCl_3$; $Me_4Si$) 18.26, 47.90, 111.54, 113.28, 117.90, 122.93, 124.89, 127.66, 127.88, 129.07, 138.30, 143.38, 143.70, 147.52, 152.17, 157.17; *m/z* (EI) 346 ($M^+$, 42%) 196 ($M^+ - N_2C_6H_4NO_2$, 38), 91 ($C_6H_5CH_2^+$, 100).
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