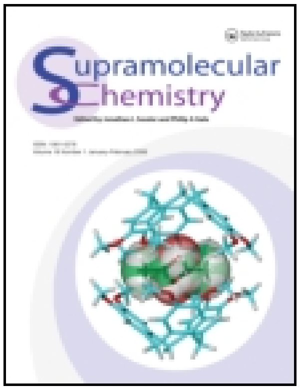

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A colorimetric anion sensing system utilising competitive C—H···X$^-$ hydrogen bonding

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Combination of tripodal imidazolium-based anion receptor **1** and azonia betaine dye **2** has enabled a colorimetric detection of halide ions by competitive binding. The imidazolium groups of receptor **1** interact with the phenoxy oxygen of betaine dye **2** in acetonitrile solution by multiple [C—H···O$^-$] hydrogen bonds. Consequently, the blue-coloured solution of the dye immediately turns to greenish yellow upon addition of receptor **1** due to the receptor–dye complex formation. The reversed colour change, which is caused by displacement of guests, is observed by the addition of Cl$^-$, Br$^-$ or I$^-$ anions to the receptor–dye complex solution.

Keywords: anion recognition; imidazolium; competitive binding; C—H hydrogen bonding; colorimetric anion sensing

1. Introduction

During the last decade, there has been a considerable interest in developing systems capable of recognising, sensing and transporting anionic species (*1*). Especially, the development of chromogenic anion receptors or colorimetric anion sensing systems, which generally consist of covalently linked anion-binding sites, and chromophores is an important issue because they can be monitored by the naked eyes providing instant qualitative information without any instruments and they can produce optical sensors for quantitative analysis (*2*).

1,3-Disubstituted imidazolium group is an effective anion binding unit, and we discovered that the tripodal imidazolium-based receptor **1** shows a high binding affinity for halide ions in polar solvents by electrostatic interaction together with [C—H···X$^-$] hydrogen bond (*3*). Recently, imidazolium (*4*) and other related C—H hydrogen-bonding-type anion receptors (*5–9*) have attracted interest for a wide variety of research purposes from fundamental anion coordination studies to analytical applications.

Although a number of fluorescent probes for anion detection based on imidazolium receptors have been reported (*10*), a colorimetric imidazolium-based anion receptor is still very rare (*11–13*). An alternative method to a covalently attached chromophore is a competition binding between an indicator and a target analyte to a receptor. The indicator is displaced from the binding site of the receptor upon addition of competitive analytes, causing a signal modulation (*2*). Anslyn and his co-workers (*14*) addressed the displacement method for the detection of biologically important species, and verified and demonstrated the advantage of this method. Gale and his co-workers (*15*) also have applied this method to a calix[4]pyrrole-type receptor with tetrabutylammonium 4-nitrophenolate as an indicator for colorimetric detection of fluoride anion.

To create a sensitive colorimetric response, the indicator must cause a substantial absorption change upon addition to the receptor (*2*). However, the combination of imidazolium-based receptors with typical hydrogen-bond accepting indicators, such as *N*,*N*-dimethylindoaniline (phenol blue) or bis-4,4′-(*N*,*N*-dimethylamino)benzophenone (Michler's ketone), did not show any significant colour change, because the relatively weak C—H hydrogen bonding of the imidazolium unit not only had strong affinity for the neutral indicators but also gave small perturbation to the electronic structure of the indicators. Thus, more sensitive hydrogen-bond accepting indicators are required. We investigated the use of a merocyanine-type azonia betaine dye **2**, which was developed in our laboratory for an indicator of solvent polarity (*16*, *17*), as an indicator for the displacement method.

Here, we report a colorimetric anion sensing system by applying the displacement methodology to imidazolium-based anion receptor **1** coupled with azonia betaine dye **2** (Scheme 1).

2. Results and discussion

The imidazolium-based tripodal receptor **1** and azonia betaine dye **2** used were synthesised as described previously (*3*, *17*).

In slightly basic acetonitrile solution (containing 0.4% piperidine), solvatochromic azonia betaine dye **2** shows a characteristic deep blue colour. The addition of **1**

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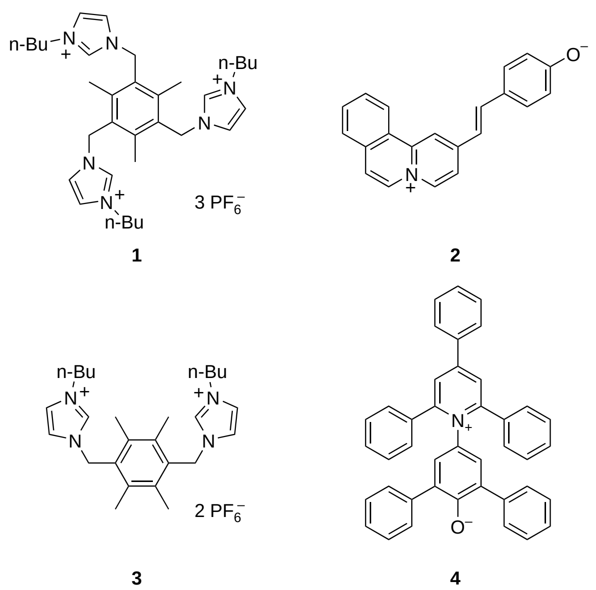

Scheme 1. Structure of receptors (**1**, **3**) and dyes (**2**, **4**).

(8.0×10^{-5} mol dm^{-3}) to an acetonitrile solution of dye **2** (1.0×10^{-5} mol dm^{-3}) at room temperature caused a significant decrease in the intensity of intramolecular charge-transfer absorbance band at 622 nm and an increase in absorbance band at 422 nm, with an isosbestic point around 510 nm (Figure 1). The absorbance ratio of the two bands was dependent on the concentration of receptor **1** added, which indicates the formation of a host–guest complex in the solution.

To obtain the structural evidence relating to the complex between receptor **1** and dye **2**, ^{1}H NMR spectroscopic investigation was performed. The spectrum of the 1:1 mixture of **1** and **2** in CD$_3$CN (each concentration being 1.0×10^{-3} mol dm^{-3}) shows a 0.57 ppm downfield shift of the imidazolium C(2)—H proton of **1** compared to the chemical shift of **1** in the absence of **2**. This result clearly indicates that receptor **1** and dye **2** form a complex in the solution and the observed colour change, from blue to greenish yellow, is attributed to the formation of multiple hydrogen bonds between imidazolium C(2)—H proton of **1** with the highly electronegative phenolate oxygen atom of the merocyanine-type betaine dye **2**.

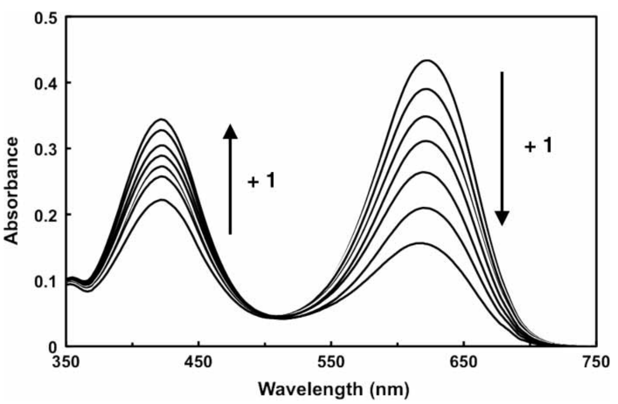

Figure 1. Spectral change of the azonia betaine dye **2** (1.0×10^{-5} mol dm^{-3}) upon addition of tripodal imidazolium receptor **1** (0–8.0×10^{-5} mol dm^{-3}) in acetonitrile (containing 0.4% piperidine).

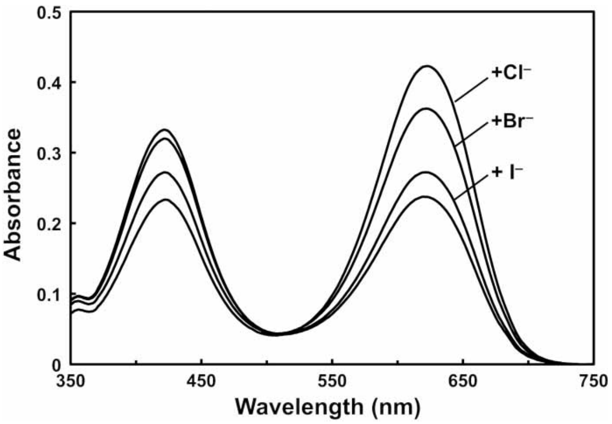

Figure 2. Chromogenic response of complex **1** and **2** to Cl$^-$, Br$^-$ and I$^-$ (tetraethylammonium salts) in acetonitrile (containing 0.4% piperidine). [**1**] = 4.0×10^{-5} mol dm^{-3}, [**2**] = 1.0×10^{-5} mol dm^{-3} and [anion] = 4.0×10^{-4} mol dm^{-3} at 25°C.

We also investigated Reichardt's pyridinium *N*-phenoxide dye **4** (*18*), a typical solvatochromic dye having a similar betaine structure, instead of dye **2**. However, dye **4** did not show any spectral change upon addition of **1** under the same condition, probably because a steric hindrance of 2,6-phenyl groups of **4** prevents the phenolate oxygen atom from forming hydrogen bonds with receptor **1**.

On the other hand, the spectrum of dye **2** was not affected by the addition of 1,3-dimethylimidazolium hexafluorophosphate and a dipodal imidazolium-based receptor **3** (*20*).

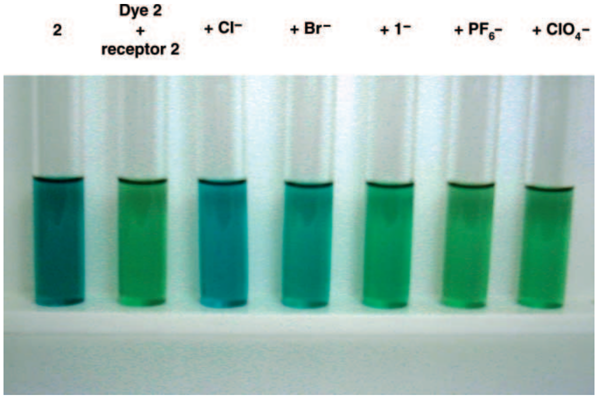

Figure 3. Colour changes of an acetonitrile solution (containing 0.4% piperidine) of **2** with **1** and after addition of halide anions to a solution of complex **1** and **2**. [**1**] = 1.6×10^{-4} mol dm^{-3}, [**2**] = 0.2×10^{-4} mol dm^{-3} and [anion] = 5.0×10^{-4} mol dm^{-3} at 25°C.

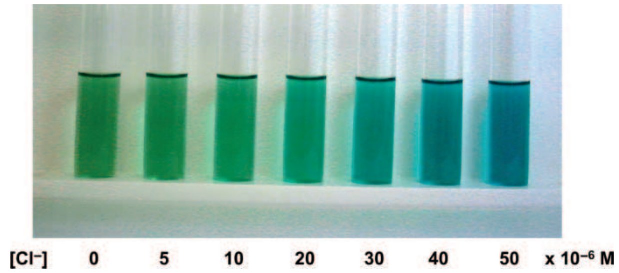

Figure 4. Colorimetric analysis of Cl^- in acetonitrile (containing 0.4% piperidine). $[\mathbf{1}] = 16 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$, $[\mathbf{2}] = 2 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$ and $[\mathrm{anion}] = 0\text{–}50 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$ at 25°C.

The binding constants between these imidazolium derivatives and betaine dye **2** are not enough to form a hydrogen-bonded complex in the same concentration range.

The binding constant K between **1** and **2** was determined by the UV–vis titration experiment (*19*). Rose-Dorago analysis of the titration data gave $K = 9.51 \times 10^4\ \mathrm{dm^3\,mol^{-1}}$. A previous study showed that Cl^- and Br^- ions bind to receptor **1** with binding constants of 7.5×10^4 and $4.6 \times 10^4\,\mathrm{dm^3\,mol^{-1}}$, respectively (*3*). Thus, the binding ability of tripodal receptor **1** for betaine dye **2** is competitive with these halide anions and has a suitable strength for use in displacement assays.

Competition experiments with Cl^-, Br^- and I^- anions were performed with a solution of receptor **1** and dye **2** (concentrations of **1** and dye **2** being 4.0×10^{-5} and $1.0 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$, respectively) (Figure 2). By addition of tetraethylammonium chloride to the solution, the reversed colour change is observed. The regenerated blue colour was attributed to the increasing proportion of the free betaine dye in the solution.

Although addition of tetraethylammonium bromide and iodide anions also causes a similar spectral change, the ratios of the two absorption bands (622 nm vs. 422 nm) at the same anion concentration ($4.0 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$) are smaller than that for chloride. Control experiments with hexafluorophosphate and perchlorate anions did not show a similar spectral change. The observed difference reflects to the binding ability of **1**.

The binding constants for receptor **1** and halide anions were determined according to competitive UV–vis spectroscopic titration studies (*19*). The calculated binding constants are $6.5 \times 10^4\,\mathrm{dm^3 mol^{-1}}$ (for Cl^-), $1.7 \times 10^4\,\mathrm{dm^3 mol^{-1}}$ (for Br^-) and $6.8 \times 10^3\,\mathrm{dm^3\,mol^{-1}}$ (for I^-), respectively, and the values are consistent with the previous data obtained by ^1H NMR titration studies (*3*) within experimental errors. These results support that the response of the observed colour changes towards anion is predominantly dependent on the anion affinity of receptor **1**.

The demonstration of a colorimetric analysis using receptor **1** and dye **2** is shown in Figures 3 and 4 (full colour pictures are available online).

3. Conclusion

In summary, we have demonstrated a visual colour sensing of halide anions using competition assays involving the C—H hydrogen bonding between imidazolium and betaine dye. The present results provide a guideline for designing more efficient colorimetric imidazolium-based anion receptors. Further studies of various imidazolium-based receptors and chromic dye systems are currently continued in our laboratory.

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