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Selective anion sensing based on a dual-chromophore approach†

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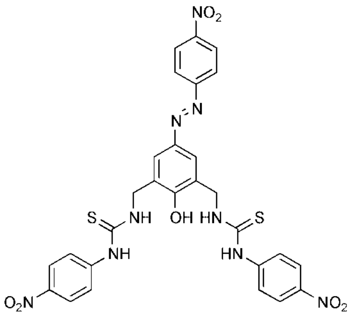
A new anion sensor 1 with an azophenol and *p*-nitrophenyl moieties as chromophores allows for easy colorimetric differentiation of F^-, $H_2PO_4^-$ and AcO^- with similar basicity.

Currently, the development of receptors for biologically important anions is emerging as a research area of great importance.[1] One of the more attractive approaches in this field involves the construction of chemosensors.[2–4] This kind of system is generally composed of two parts. One is the anion-binding part employing various combinations of pyrroles, guanidiniums, Lewis acids, amides and urea/thioureas.[1–5] The other is the chromophore which turns binding-induced changes into optical signals.[2–4] These two parts are either covalently attached[4] or intermolecularly linked.[2a,b,3] Previously, we presented a new chromogenic azophenol–thiourea based anion sensor which allows for the colorimetric detection of F^-, $H_2PO_4^-$ and AcO^-.[6] However, this system is not able to discriminate between $H_2PO_4^-$, AcO^- and F^-.



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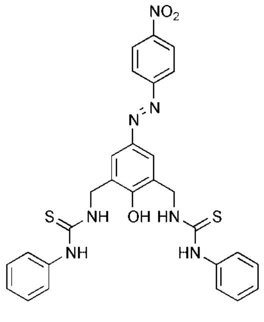

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We now present a dual-chromophore anion sensor **1** with *p*-nitrophenylazophenol[1a,7] and *p*-nitrophenylthiourea moieties as two different chromophores.[8] The anion recognition *via* hydrogen-bonding interactions can be easily monitored by anion-complexation induced changes in UV-vis absorption spectra and with the naked eye.

Synthesis of sensors **1** and **2** is described in the ESI†.[6,7,9a] **1** and **2** contain four thiourea NH groups as hydrogen-bonding donors for anions[9b] and one azophenol OH group as both an additional binding site and a color-monitoring unit.[6] In the case of **1**, the introduction of a *p*-nitrophenyl group to the thiourea moiety as another chromophore enables color differentiation of anions in a cooperative manner, along with an azophenol group upon anion binding. This approach brings together changes in λ_{max} of two chromophores to render colorimetric detection of anions more effective than with only one chromophore.

It turns out that the UV-vis absorption band of **1** in chloroform undergoes a red shift as a phosphate anion is bound. In the absence of anions, the spectrum of **1** is characterized by the presence of one absorption maximum at 339 nm. Upon addition of increasing amounts of $H_2PO_4^-$, the peak at 339 nm decreases while the new peaks gradually move to longer wavelengths finally reaching maximum values at 374 nm (due to a *p*-nitrophenyl group) and 538 nm (due to an azophenol group) (Fig. S1a). Complexation with a series of anions results in similar red shift tendencies. Clear isosbestic points are observed, which demonstrates the existence of two states of a 1 : 1 complex. As can be expected from the UV-vis data, color change occurs through addition of anions to the solution of **1**. Upon the addition of $H_2PO_4^-$, the color of the solution changes from light yellow to violet. The color change terminates after the addition of 40 equiv. of $H_2PO_4^-$. However, in the case of HSO_4^-, Cl^- and Br^-, no detectable color changes are observed upon excess addition of anions to the solution of **1**.

The qualitative changes explained above are reflected in the quantitative data in the UV-vis absorption experiment. In these chromophores, electronic excitation generally occurs through a charge transfer from the donor oxygen of the azophenol and donor nitrogen of the thiourea to the acceptor substituent ($-NO_2$) of each chromophore. Upon the complex formation of **1** with an anion, the excited state would be more strongly stabilized by anion binding, resulting in a bathochromic shift in λ_{max}.[8] The color discrimination comes from different λ_{max} values in each complex and the relative contribution of the two chromophores (Fig. 1).

The degree of a red shift for **1** was determined to be $H_2PO_4^- \gg AcO^- \approx F^- > Br^- \approx Cl^- > HSO_4^- \approx I^-$. The maximum red-shift value (λ_{max} = 538 nm) for $H_2PO_4^-$ can be understood on the basis of the guest basicity and structure of the complex. According to the basicity of anions,[9b,10] $H_2PO_4^-$, F^- and AcO^- give stronger complexes and thus show noticeable color changes compared to other anions. $H_2PO_4^-$ with four oxygens affects both chromophores *via* multitopic hydrogen bonds to give rise to a pronounced color change, while F^- and AcO^- have a relatively weaker effect on the *p*-nitrophenyl group with respect to inducing color changes. This enables color discrimination between $H_2PO_4^-$, F^- and AcO^-. In the case of sensor **2** with only an azophenol group as the chromophore, λ_{max} values upon complexation with $H_2PO_4^-$, F^- and AcO^- are similar

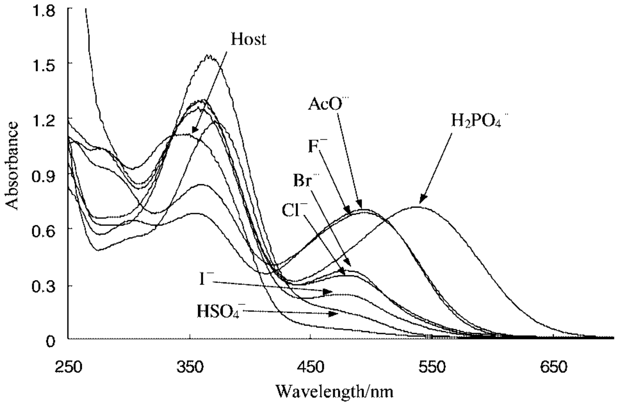

Fig. 1 UV-vis changes of **1** operated in $CHCl_3$ (5.0×10^{-5} M) after the addition of 40 equiv. of anions.

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† Electronic supplementary information (ESI) available: experimental details for **1** and **2**, Figs. S1 and S2. See http://www.rsc.org/suppdata/cc/b1/b102187g/

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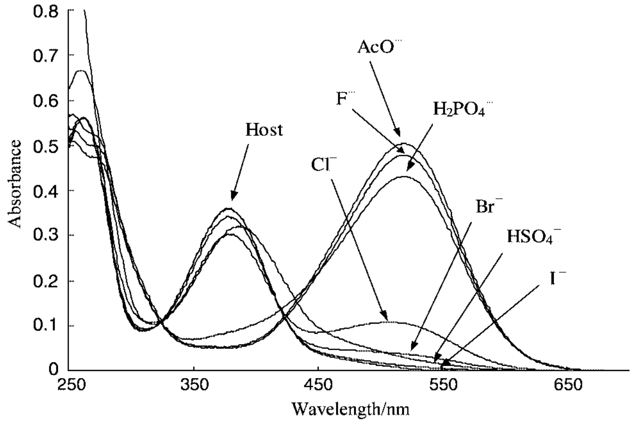

Fig. 2 UV-vis changes of **2** operated in $CHCl_3$ (1.5×10^{-5} M) after the addition of 40 equiv. of anions.

(Fig. S1b and Fig. 2) and thus the color differentiation between $H_2PO_4^-$, F^- and AcO^- is not feasible. This means that the cooperativity of dual-chromophores enables color discrimination of anions $H_2PO_4^-$, F^- and AcO^- with similiar basicity. Considering that an azophenol on its own does not exhibit color changes through addition of anions except for F^-,[11] this result indicates that the introduction of *p*-nitrophenylthiourea groups as an anion-binding site increases the electronic interaction between **1** and the anion, and furthermore results in color discrimination between $H_2PO_4^-$, F^- and AcO^-.

In summary, we have developed a new anion sensor **1** with azophenol and *p*-nitrophenyl moieties as two chromophores. This dual-chromophore system allows for colorimetric differentiation of $H_2PO_4^-$, F^- and AcO^- with similar basicity.

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