

Selective anion sensing based on a dual-chromophore approach†

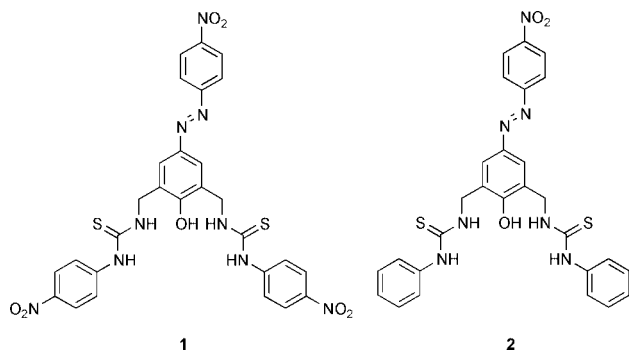
Dong Hoon Lee,^a Ho Yong Lee,^a Kwan Hee Lee^a and Jong-In Hong^{*ab}^a School of Chemistry and Molecular Engineering, Seoul National University, Seoul 151-742, South Korea. E-mail: jihong@plaza.snu.ac.kr^b Center for Molecular Design and Synthesis, KAIST, Taejeon 305-701, Korea

Received (in Cambridge, UK) 7th March 2001, Accepted 22nd May 2001

First published as an Advance Article on the web 14th June 2001

A new anion sensor **1** with an azophenol and *p*-nitrophenyl moieties as chromophores allows for easy colorimetric differentiation of F⁻, H₂PO₄⁻ 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 attached⁴ 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⁻, H₂PO₄⁻ and AcO⁻.⁶ However, this system is not able to discriminate between H₂PO₄⁻, AcO⁻ and F⁻.



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 H₂PO₄⁻, 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 H₂PO₄⁻, the color of the solution changes from light yellow to violet. The color change terminates after the addition of 40 equiv. of H₂PO₄⁻. However, in the case of HSO₄⁻, 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 (-NO₂) 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 H₂PO₄⁻ ≫ AcO⁻ ≈ F⁻ > Br⁻ ≈ Cl⁻ > HSO₄⁻ ≈ I⁻. The maximum red-shift value (λ_{max} = 538 nm) for H₂PO₄⁻ can be understood on the basis of the guest basicity and structure of the complex. According to the basicity of anions,^{9b,10} H₂PO₄⁻, F⁻ and AcO⁻ give stronger complexes and thus show noticeable color changes compared to other anions. H₂PO₄⁻ 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 H₂PO₄⁻, F⁻ and AcO⁻. In the case of sensor **2** with only an azophenol group as the chromophore, λ_{max} values upon complexation with H₂PO₄⁻, F⁻ and AcO⁻ are similar

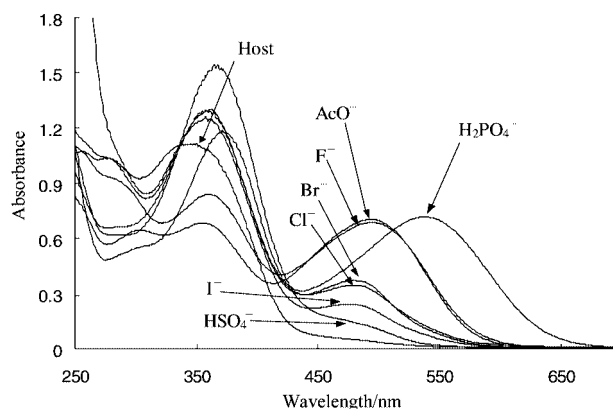


Fig. 1 UV-vis changes of **1** operated in CHCl₃ (5.0 × 10⁻⁵ M) after the addition of 40 equiv. of anions.

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

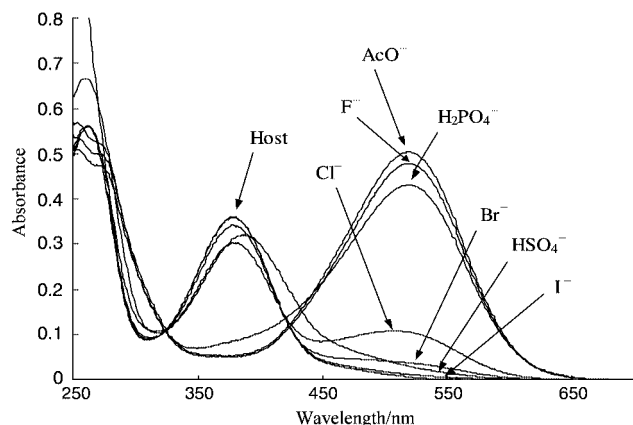


Fig. 2 UV-vis changes of **2** operated in CHCl_3 (1.5×10^{-5} M) after the addition of 40 equiv. of anions.

(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 similar 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.

Financial support from the KRF (Grant No. KRF-99-042-D00073) is gratefully acknowledged. We thank the

Ministry of Education (BK 21 program) for a postdoctoral fellowship awarded to K. H. L., and predoctoral fellowships awarded to H. Y. L. and D. H. L.

Notes and references

- (a) *Comprehensive Supramolecular Chemistry*, Chair ed. J.-M. Lehn, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle, Pergamon, Oxford, 1996, Vol. 1; (b) *Chemosensors of Ion and Molecular Recognition*, ed. J.-P. Desvergne and A. W. Czarnik, Kluwer, Dordrecht, 1997, Vol. 492; (c) F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609.
- (a) K. Niikura and E. V. Anslyn, *J. Am. Chem. Soc.*, 1998, **120**, 8533; (b) A. Metzger and E. V. Anslyn, *Angew. Chem., Int. Ed.*, 1998, **37**, 649; (c) Y. Kubo, S. Maeda, S. Tokita and M. Kubo, *Nature*, 1996, **382**, 522.
- (a) J. J. Lavigne and E. V. Anslyn, *Angew. Chem., Int. Ed.*, 1999, **38**, 3666; (b) P. A. Gale, L. J. Twyman, C. I. Handlin and J. L. Sessler, *Chem. Commun.*, 1999, 1851.
- (a) C. B. Black, B. Andrioletti, A. C. Try, C. Ruiperez and J. L. Sessler, *J. Am. Chem. Soc.*, 1999, **121**, 10438; (b) H. Miyaji, W. Sato and J. L. Sessler, *Angew. Chem., Int. Ed.*, 2000, **39**, 1777; (c) P. Anzenbacher, K. Jursíková and J. L. Sessler, *J. Am. Chem. Soc.*, 2000, **122**, 9350.
- For reviews, see (a) *Supramolecular Chemistry of Anions*, ed. A. Binachi, K. Bowman-James and E. Garcia-España, Wiley-VCH, New York, 1997; (b) *Supramolecular Chemistry, Concepts and Perspectives*, ed. J. M. Lehn, Wiley-VCH, Weinheim, 1995.
- D. H. Lee, K. H. Lee and J.-I. Hong, *Org. Lett.*, 2001, **3**, 5.
- A. Tsuge, T. Moriguchi, S. Mataka and M. Tachiro, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2211.
- S. Nishizawa, R. Kato, T. Hayashita and N. Teramae, *Anal. Sci.*, 1998, **14**, 595.
- (a) M.-S. Muche and M. W. Göbel, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2126; (b) S. Nishizawa, P. Bühlmann, M. Iwao and Y. Umezawa, *Tetrahedron Lett.*, 1995, **36**, 6483.
- T. R. Kelly and M. H. Kim, *J. Am. Chem. Soc.*, 1994, **116**, 7072.
- K. H. Lee and J.-I. Hong, *Tetrahedron Lett.*, submitted.