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An anion sensor based on the displacement of 2,6-dichlorophenol-indo-*o*-cresol sodium salt from a water-soluble tetrasulfonated calix[4]arene

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ABSTRACT

A colorimetric displacement assay system for F^- and $H_2PO_4^-$ anions based on a 2,6-dichlorophenol-indo-*o*-cresol sodium salt:calix[4]arene-*p*-sulfonate complex was studied in 1:1 DMSO:water solution. When calix[4]arene-*p*-sulfonate formed the complex with the blue 2,6-dichlorophenol-indo-*o*-cresol sodium salt dye, the absorption peak of the dye at 625 nm disappeared and the DMSO:water solution of the complex was colourless. However, the initial blue colour of the dye returned with the addition of both F- and $H_2PO_4^-$ anions which bound to the calix[4]arene-*p*-sulfonate and, in doing so, displaced the 2,6-dichlorophenol-indo-*o*-cresol sodium salt from the 2,6-dichlorophenol-indo-*o*-cresol:calix[4]arene-*p*-sulfonate complex. The findings imply that this displacement assay could be used to develop potential optical signalling systems for the detection of anions such as F^- and $H_2PO_4^-$.

1. Introduction

The development of colorimetric signalling chemosensors for the selective recognition of anions has received considerable attention in recent decades owing to their key role in host-guest chemistry, especially from both biological and environmental perspectives [1]. The molecular design of chemosensing receptor system is an additional interesting area in anion recognition chemistry. The chemosensing effect involves binding a specific target anion (A^-) to receptor molecules (R) as a result of which, the chemosensor chromophore displays changes of optical signal (e.g. absorbance) owing to the formation of a receptor:sensing anion complex, namely R:A^-. As F^- is the smallest anion and has unique biological and chemical properties, its recognition and detection are of great interest because of its well known usage in dental care [2,3] and osteoporosis [4] as well as its potentially damaging nephrotoxic effect in humans that can result from overly high concentrations of fluoride [5].

Useful receptor molecules that are capable of detecting anions have been prepared which involve the use of hydrogen bonds either alone or in conjunction with other electrostatic interactions, to provide binding sites for anionic species. Chromogenic signalling systems that provide a vivid colour change upon anion complexation have been shown to offer potential for target anion detection with the naked-eye [6–9]. Anslyn et al. utilised a displacement assay approach based on the interaction of a guanidinium containing receptor with citrate anions [10]. A further colorimetric displacement assay system based on competition between anions and merocyanine dyes towards calix[4]pyrrole was reported by Machado et al. [11], the chemosensing effect resulting from complex formation between a phenolate donor in the merocyanine dye and –NH pyrrole groups in calix[4]pyrrole. Calixarenes are phenolic metacyclophanes annulated by single methylene groups [15]. There are five members of the series, ranging from the relatively rigid tetrameric calix[4]arene to the much larger and more flexible, octameric calix[8]arene. Owing to their cavity-shaped molecular architecture, calixarenes have been widely employed as building blocks in the design of novel host molecules [16].

This paper concerns the formation of a colorimetric displacement assay (**3**) system based upon the H-bond interaction between calix[4]arene-*p*-sulfonate (**1**) and 2,6-dichlorophenol-indo-*o*-cresol

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sodium salt (DIC, **2**), which can operate in 1:1 DMSO:water solution and which shows selectivity for both F^- and $H_2PO_4^-$ anions.

2. Experimental

Calix[4]arene-*p*-sulfonate (**1**) and 2,6-dichlorophenol-indo-*o*-cresol sodium salt (DIC, **2**) were purchased from Aldrich. All chemicals, including the tetrabutylammoniun salts of various anions, namely F^-, $H_2PO_4^-$, NO_3^-, HSO_4^-, ClO_4^-, Br^- and Cl^- and solvents were of the highest purity grade available and were used without further purification. UV–Vis spectra were measured using an *Agilent 8453* spectrophotometer.

To study the displacement assay system of the DIC:calix[4]arene-*p*-sulfonate complex (**3**), the addition of 0–8 equiv of calix[4]arene-*p*-sulfonate to a 1×10^{-4} M, 1:1 DMSO:distilled water solution of DIC was monitored using UV–Vis spectrophotometry. In addition, UV–Vis spectra were also determined for the addition of 0–2 equiv of tetrabutylammonium fluoride to a 1:1 DMSO:water solution containing both 1.0×10^{-4} M 2,6-dichlorophenol-indo-*o*-cresol sodium salt and 1.2×10^{-4} M calix[4]arene-*p*-sulfonate. The effect of adding different amounts of tetrabutylammonium fluoride to a DMSO:water solution of DIC:calix[4]arene-*p*-sulfonate complex was monitored spectrophotometrically.

3. Results and discussion

The dye used in this work, namely 2,6-dichlorophenol-indo-*o*-cresol sodium salt (DIC, **2**), was selected on the basis of its intramolecular charge transfer characteristics and was utilized as a chemosensor because of its ability to bind calix[4]arene-*p*-sulfonate in aqueous media. The donor-acceptor system of the dye resembles that of Reichardt's well known solvatochromic, betain dye, 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate, which has often been used to determine the polarity of an aqueous media [12,13]. In this context, Machado and co-workers reported an anionic chromogene sensor based on protonated Reichardt's dye [14].

It is known that the addition of compounds that posses –OH groups to an aq. solution of Brooker's merocyanine or Reichardt's dye imparts a hypsochromic shift in λ_{max} due to the formation of H-bonds between the O^- donor moiety in the dye and the –OH group of the added compound [11,17]. In this context, a 1:1 DMSO:water solution of DIC is blue coloured and it was expected that the addition of the water-soluble calix[4]arene-*p*-sulfonate (**1**) would lower the absorbance of the dye at λ_{max} (625 nm), changing the colour of the dye solution as a result of the formation of the H-bonded DIC:calix[4]arene-*p*-sulfonate complex (**3**).

Fig. 2(a) shows the changes in the absorption spectra of the originally blue coloured solution of 1×10^{-4} M DIC in 1:1 DMSO:water imparted by the addition of 0–8 equivalents of calix[4]arene-*p*-sulfonate, from which it is apparent that the absorbance of the dye at 625 nm gradually decreased with increasing concentration of calix[4]arene-*p*-sulfonate and the color of the solution changed from blue to colourless. The stoichiometry of the DIC:calix[4]arene-*p*-sulfonate complex was 1:1.5 (Fig. 2(a). inset), which is schematically illustrated in Fig. 1.

It was further anticipated that the subsequent addition of anions to the colourless DMSO:water solution of DIC:calix[4]arene-*p*-sulfonate complex would return the dye's original blue color, owing to the displacement of DIC from the complex (Fig. 1). As shown in Fig. 2(b), the absorbance at 625 nm increased with increasing amount of fluoride anion that was added to a solution of the DIC:calix[4]arene-*p*-sulfonate complex. The original blue color of the DIC returned with the addition of tetrabutylammonium fluoride, which bound selectively to the calix[4]arene-*p*-sulfonate receptor and displaced the DIC. The intensity of the blue colour imparted by the addition of F^- anions was high enough to be detected by the naked-eye.

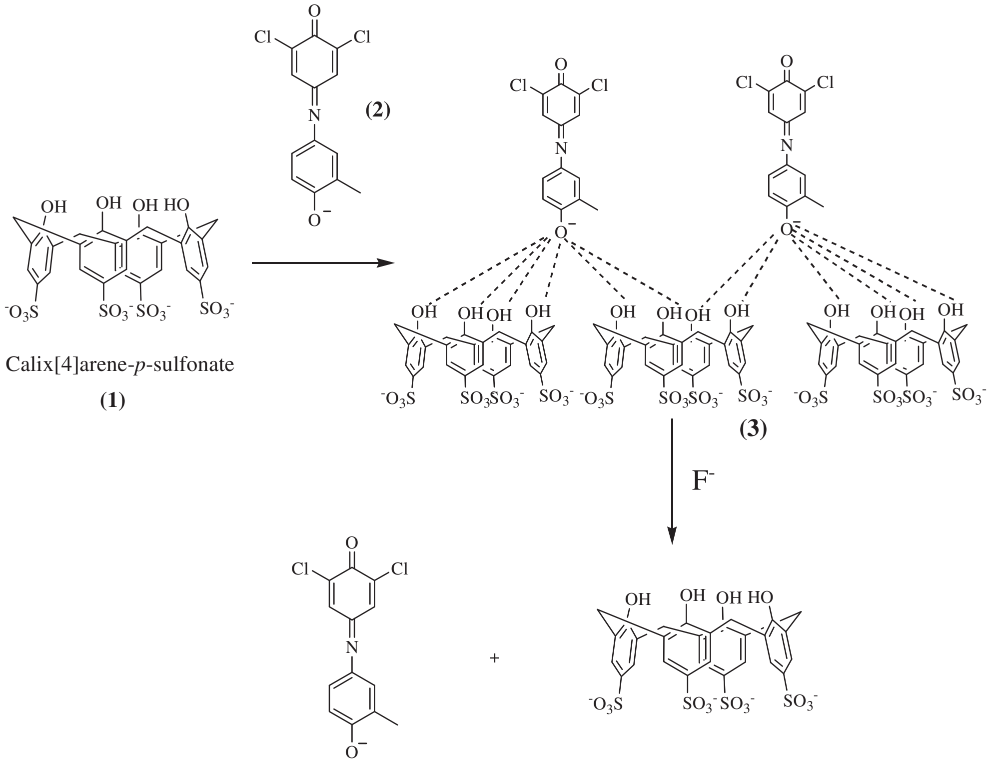

Fig. 1. Schematic illustration of a displacement assay chemosensor based on DIC:calix[4]arene-*p*-sulfonate complex.

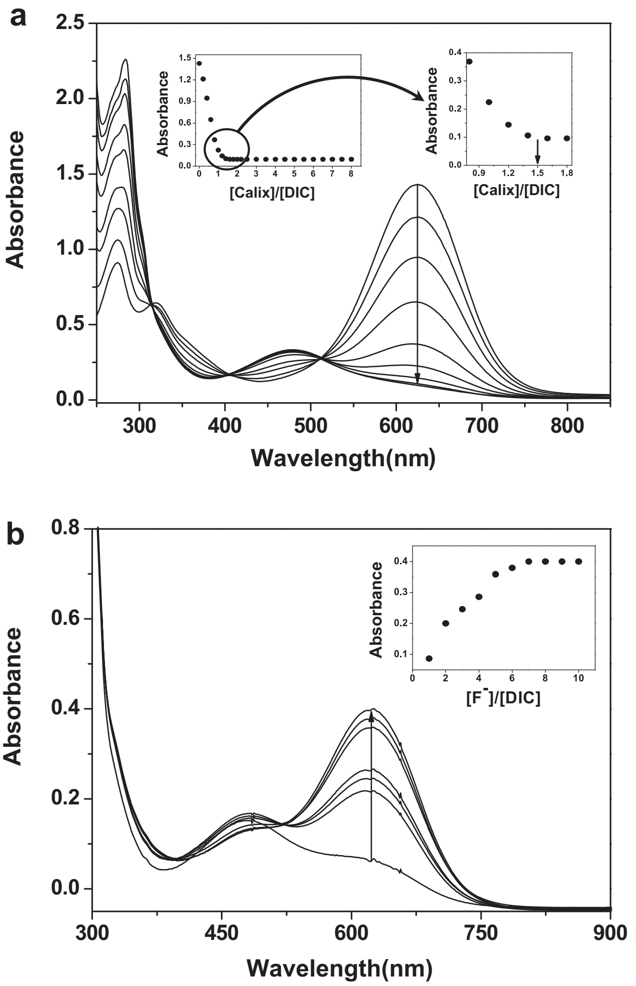

Fig. 2. UV–Vis spectra of DIC (a) addition of 0–8 equiv of calix[4]arene-*p*-sulfonate to 1:1 DMSO:water solution of 1.0 × 10^{-4} M DIC and (b) addition of 0–2 equiv of tetrabutylammonium fluoride to 1:1 DMSO:water solution containing both 1.0 × 10^{-4} M DIC and 1.2 × 10^{-4} M calix[4]arene-*p*-sulfonate; inset shows the absorbance at 625 nm as a function of $[F^-]$.

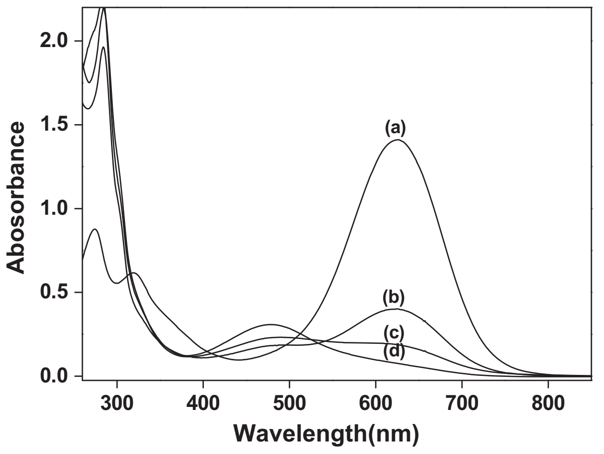

Fig. 3. UV–Vis spectra of 1:1 DMSO:water solution of (a) 1.0 × 10^{-4} M DIC, (b) DIC:calix[4]arene-*p*-sulfonate (1.0 × 10^{-4} M DIC and 1.2 × 10^{-4} M calix[4]arene-*p*-sulfonate) as well as DIC:calix[4]arene-*p*-sulfonate (1.0 × 10^{-4} M DIC and 1.2 × 10^{-4} M calix[4]arene-*p*-sulfonate) in the presence of (c) 1.0 × 10^{-4} M $H_2PO_4^-$ and (d) 1.0 × 10^{-4} M F^-.

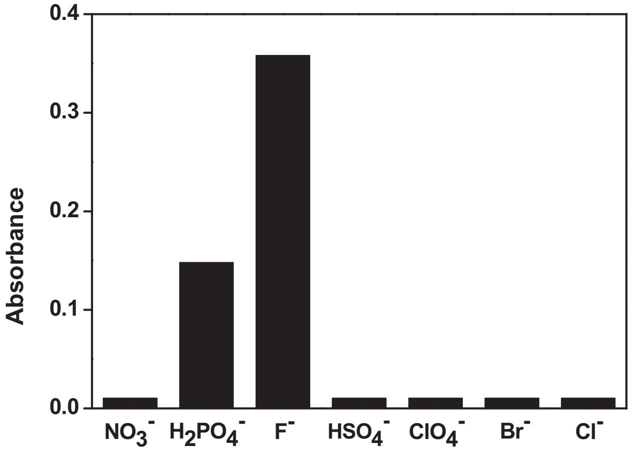

Fig. 4. Relative absorbance changes of DMSO:water solutions containing 1.2 × 10^{-4} M calix[4]arene-*p*-sulfonate, 1.0 × 10^{-4} M DIC and 1.0 × 10^{-4} M tetrabutylammoniun salts of various anions, namely F^-, $H_2PO_4^-$, NO_3^-, HSO_4^-, ClO_4^-, Br^- and Cl^-.

Fig. 3 shows the UV–vis spectra obtained for DMSO:water solutions of DIC as well as DIC:calix[4]arene-*p*-sulfonate complex alone and the DIC:calix[4]arene-*p*-sulfonate complex in the presence of 1.0 × 10^{-4} M $H_2PO_4^-$ and also 1.0 × 10^{-4} M F^- (the concentration of DIC and calix[4]arene-*p*-sulfonate were 1.0 × 10^{-4} M and 1.2 × 10^{-4} M respecively). It is evident that the addition of $H_2PO_4^-$ to the calix[4]arene-*p*-sulfonate:DIC solution resulted in a smaller absorbance recoverage at 625 nm than was observed in the case of the addition of F^-. Upon addition of $H_2PO_4^-$ and F^-, the original spectral pattern was not recovered, indicating that the DIC formed more stable complexes with calix[4]arene-*p*-sulfonate than did F^-.

Of the tetrabutylammoniun salts of various anions, namely F^-, $H_2PO_4^-$, NO_3^-, HSO_4^-, ClO_4^-, Br^- and Cl^-, it was found that only those of F^- and $H_2PO_4^-$ resulted in the reappearance of the initial peak at 625 nm of the blue dye and which could be monitored visually, when added to a DMSO:water solution of the DIC:calix[4]arene-*p*-sulfonate complex. The addition of the other anions used (NO_3^-, HSO_4^-, ClO_4^-, Br^- and Cl^-) had no significant effect on the absorption spectra (Fig. 4).

The observed reappearance of the blue color of the dye imparted by the addition of F- anions to the DIC: calix[4]arene sulfonate complex can be attributed to the marked ability of the F^- anion to associate strongly with the water-soluble calix[4]arene and, in doing so, dislodges the DIC from the receptor site of the calix[4]arene sulfonate, thereby allowing the dye to once more absorb at 625 nm and thus signal the presence of the analyte.

4. Conclusions

The mixture of water-soluble calix[4]arene with DIC in DMSO:water resulted in the formation of a colourless, host receptor–dye anion complex which acted as a chromogenic anion sensor. The findings imply that this particular displacement assay system offers potential application for the development of optical signalling systems for the detection of anions such as F^- and $H_2PO_4^-$.

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References

[1] (a) Spichiger-Keller Ursula. Chemical sensors and biosensors for medical and biological applications. Weinheim, Germany: Wiley-VCH; 1998;
(b) Paul DB, Elizabeth JH. Transition metal and organometallic anion complexation agents. Coordination Chemistry Reviews 2003;240:167;
(c) Franz P, Schmidtchen. Michael B. Artificial organic host molecules for anions. Chemical Reviews 1997;97:1609.

[2] Yeo HM, Ryu BJ, Nam KC. A novel fluoride ion colorimetric chemosensor. Organic Letters 2008;10:2931.

[3] Kirk KL. Biochemistry of the halogens and inorganic halides. New York: Plenum Press; 1991. p. 58.

[4] Kleerekoper. The role of fluoride in the prevention of osteoporosis. Endocrinology and Metabolism Clinics of North America 1998;27:441.

[5] Wiseman A. Handbook of experimental pharmacology XX/2. Berlin: Springer-Verlg; 1970. Part 2:48–97.

[6] Saravanakumar D, Devaraj S, Iyyampillai S, Mohandoss K, Kandaswamy M. Schiff's base phenol–hydrazone derivatives as colorimetric chemosensors for fluoride ions. Tetradedron Letters 2008;49:127.

[7] Wu FY, Hu MH, Wu YM, Tan XF, Zhao YQ, Ji ZJ. Fluoride-selective colorimetric sensor based on thiourea binding site and anthraquinone reporter. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2006;65:633.

[8] Ramon MM, Felix S. New advances in fluorogenic anion chemosensors. Journal of Fluorescence 2007;15:267.

[9] Thorfinnur G, Mark G, Gillian M, Tocci, Paul EK, Frederick MP. Anion recognition and sensing in organic and aqueous media using luminescent and colorimetric sensors. Coordination Chemistry Reviews 2006;250:3094.

[10] Axel M, Eric VA. A Chemosensor for citrate in beverages. Angewandte Chemie International Edition 1998;37:649.

[11] Monica ML, Daysi CP, Vanderlei GM. An anionic chromogenic sensor based on the competition between the anion and a merocyanine solvatochromic dye for calix[4]pyrrole as a receptor site. Tetrahedron Letters 2007;48:4547.

[12] Reichardt C. Solvents and solvent effects in organic chemistry. New York: VCH Publishers; 1988.

[13] Reichardt C. Solvatochromic dyes as solvent polarity indicators. Chemical Reviews 1994;94:2319.

[14] Dalci CR, Clodoaldo M, Vanderlei GM. An anionic chromogenic sensor based on protonated Reichardt's pyridiniophenolate. Tetrahedron Letters 2006;47:9339.

[15] Gutsche CD. Calixarenes. Cambridge: The Royal Society of Chemistry; 1986.

[16] Vicens J, Bohmer V. Calixarenes. Dordrecht: Kluwer Academic; 1990.

[17] Dawber JG, Williams RA. A nuclear magnetic resonance study of the solvatochromism of a pyridinium betaine. Journal of the Chemical Society, Faraday Transactions 1 1986;82:3097.