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A high selective anion colorimetric sensor based on salicylaldehyde for fluoride in aqueous media

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ABSTRACT

A new and simple salicylaldehyde-based sensor 1 designed for fluoride sensing has been investigated in DMSO and even in the 9/1 DMSO/H_2O (v/v) mixtures. The affinity constants of receptor 1 for anionic species in the 9/1 DMSO/H_2O (v/v) reveal that it is sensitive to F. Also, the color changes induced by anions can provide a way of detection by 'naked-eye'. These result can be substantiated by the spectrum changes upon the addition of 25 equiv. anions to 1 in the 9/1 DMSO/H_2O solution. The further insights to the nature of interactions between the sensor 1 and F^- were investigated by ^1H NMR titration experiments in 9/1 DMSO-d_6/H_2O (v/v). In addition, the proposed binding mode between 1 and F^- was suggested.

1. Introduction

Over the past few years, the recognition of inorganic and biotic anions have been a key research area of supramolecular chemistry [1,2] owing to the fundamental role of anions in the environment and biological systems, and in the clinic practices and so on. Despite their popularity in biological system, the design of 'substrate specific' synthetic receptors still reveals a great challenge due to (1) the large size of anions compared to the cations, (2) the chemical environment that determines the strength of interaction, and (3) the pH of the medium. Thus, the development of designing anion receptors is crucial and emergent.

One of the frequently used strategies to design anion sensors involves the constructions of optical receptors [3–5]. Such systems are generally composed of anion binding sites and the chromogenic moieties. When anions interact with the sensor via electrostatic, hydrogen bonding, coordination to a metal center, hydrophobic interaction, or a combination of any two or more of these interactions, the sensor can output binding information either by its altered fluorescence, absorption spectra or both behaviours [6–8].

Recently, among the range of biologically important anions, fluoride is of particular interest owing to its serious effects in the human body [9–13]. In this connection, we found recently that many chromogenic chemosensors for fluoride were developed. For example, an effective sensor for fluoride ion in dry DMSO was reported by Cheng and co-workers [14]. The selective acetate-binding property of the fluorinated derivative of the dipyrrolyl-diketone BF_2 complex was reported by Maeda and Ito in DMSO [15]. Besides, a new series of indolocarbazole-quinoxalines were prepared and characterized for effective fluoride and acetate anion sensing in DMSO by Yan and co-workers [16].

Despite these remarkable achievements, there are still many disadvantages recognized in many examples of the literatures. For example, the recognition and/or sensing of anions could only ever occur in the biochemically noncompetitive organic solvents [17,18] (e.g. CH_3CN, CH_2Cl_2, etc.) but never in the biochemically competitive protic solvents such as H_2O, CH_3CH_2OH. Consequently, there is a need to develop receptors capable of binding anion in competitive media, which is also hoped to be simultaneously accompanied with the 'naked-eyed' detectable color changes [19].

In this paper, we designed and synthesized a new and simple salicylaldehyde-based receptor (Scheme 1), which is an organic colorimetric chemosensor. The sensing of the biologically important AcO^-, $H_2PO_4^-$ and F^- anions is achieved in DMSO solution. In particular, the sensor can selectively recognize F^- anions by naked-eye detection in aqueous solution (9/1 DMSO/H_2O (v/v)) of 1. However, highly structural similar receptors reported by Saravanakumar et al. recognize F^- only in dry acetonitrile solution [20], which reveals the merits of our designed system.

2. Experimental

2.1. Apparatus

^1H NMR spectra were obtained on a Varian UNITY Plus-400 MHz Spectrometer using tetramethylsilane (TMS) as an internal stan-

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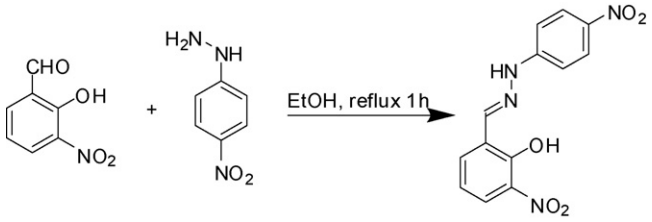


Scheme 1. General synthetic routes to the target compound 1.

dard. ESI-MS was performed with a MARINER apparatus. C, H, N elemental analyses were made on an elementar vario EL. UV–vis spectra were recorded on a Shimadzu UV2450 Spectrophotometer with a quartz cuvette (path length = 1 cm).

2.2. Reagents

Unless otherwise specified, all reagents for synthesis were obtained commercially and were used without further purification. In the titration experiments, all the anions were added in the form of tetra-n-butylammonium (TBA) salts, which were purchased from Sigma–Aldrich Chemical, stored in a vacuum desiccator containing self-indicating silica and fully dried before using. DMSO was dried with CaH_2 and then distilled in reduced pressure.

2.3. General method

All experiments were carried out at 298.2 ± 0.1 K, unless otherwise mentioned. UV–vis spectra were measured using an ultraviolet–visible spectrophotometer, UV-2450 (Shimadzu Corp., Kyoto, Japan). A 2.0×10^{-4} M solution of the compound 1 in DMSO was prepared and stored in the dry atmosphere. This solution was used for all spectroscopic studies after appropriate dilution. Solutions of 1.0×10^{-2} M tetrabutyl ammonium (TBA) salts of the respective anions were prepared in dried and distilled DMSO and were stored under a dry atmosphere.

^{1}H NMR titration experiments were carried out in the DMSO-d_6/H_2O (9/1) solution (TMS as the internal standard). The receptors prepared as 2.0×10^{-3} M solutions (DMSO-d_6/H_2O = 9/1) were titrated by the escalated amount of fluoride anion (in DMSO-d_6/H_2O = 9/1), and also ^{1}H NMR of the host–guest system was tested.

2.4. Syntheses and characterize

2.4.1. 2-Hydroxyl-3-nitro-benzaldehyde 4′-nitrophenylhydrazone (1)

0.153 g (1 mmol) 4-nitrophenylhydrazine and 0.167 g (1 mmol) 2-hydroxy-3-nitro-benzaldehyde were dissolved in 30 ml ethanol and then the resulting solution was heated and refluxed for 1 h. Precipitate formed was filtered, washed twice with ethanol (2× 5 ml) and obtained 0.294 g in 92% yield. ^{1}H NMR (DMSO-d_6, 400 MHz) δH 7.99 (d, 2H, Ar–H, J = 7.6 Hz), 8.13 (d, 1H, N = C–H, J = 8.1 Hz), 8.18 (dd, 2H, Ar–H, J = 9.3 Hz), 8.34 (s, 1H, Ar–H), 8.40 (s, 1H, Ar–H), 8.60 (s, 1H, Ar–H), 11.50 (s, 1H, N–H), 11.61 (s, 1H, O–H). ESI-mass: m/z 303.09 $(M+H)^+$. Elemental analysis calcd for $C_{13}H_{10}N_4O_5$ (M = 302.07): C, 51.66; H, 3.33; N, 18.54. Found: C, 51.75; H, 3.26; N, 18.67.

3. Results and discussion

3.1. UV–vis spectroscopy

Firstly, to evaluate the templating ability of anions, the UV–vis titration experiments of the receptor 1 were carried out in dry DMSO solution using standard tetrabutylammonium salts of AcO^-, F^-, $H_2PO_4^-$, Cl^-, Br^- and I^- at 298.2 ± 0.1 K. UV–vis spectrum of the solution of 1 (1.0×10^{-5} M) recorded upon the addition of F^- is shown (see Fig. 1). Upon the addition of F^-, the absorption peak at 430 nm was decreasing, whereas the absorption peak at 515 nm was increasing. The resulting titration revealed an isosbestic point at 445 nm.

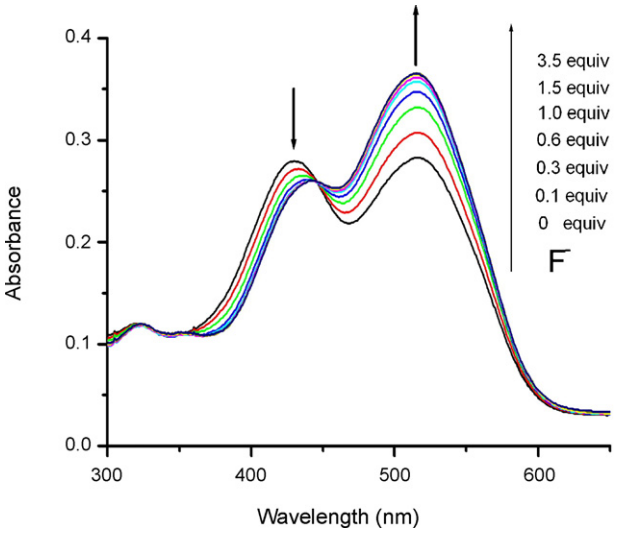


Fig. 1. UV–vis spectrum changes of receptor 1 (1.0×10^{-5} M) upon addition of fluoride ion (0–3.5 equiv.) in DMSO at 298.2 ± 0.1 K.

Secondly, to explore more about the applicability of the sensor 1 for fluoride in minor-water-containing solution, the UV–vis titrations were performed in the 9:1 DMSO/H_2O mixtures. Fig. 2 shows the UV–vis spectral changes of 1 during the titration with fluoride. The original absorbance peaks appeared at the λ_{max} of 430 nm and 502 nm, i.e. the π-π* transition bands [21] of the chromophore (nitrophenyl). With the addition of more and more doses of fluoride ions, the peak at 430 nm decreased but that at 502 nm increased, which was ascribed to the charge transfer (CT) between the anion-bound –NH and –OH units and the electron-deficient –NO_2 moiety. And the color of the sensor solution changed from yellow to red at the same time. Obviously, there was one and only one well-defined isosbestic points at 450 nm, which indicated that there existed only

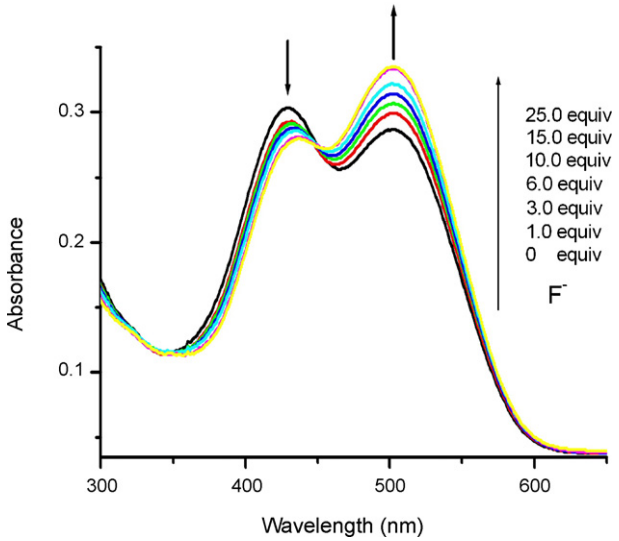


Fig. 2. UV–vis spectrum changes of receptor 1 (1.0×10^{-5} M) upon addition of fluoride ion (0–25 equiv.) in DMSO/H_2O (9/1) at 298.2 ± 0.1 K.

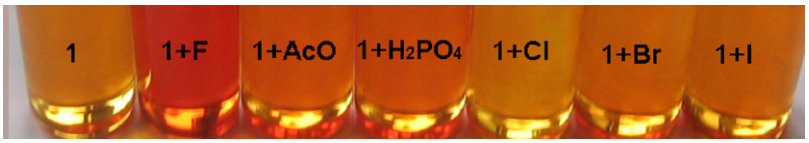


Fig. 3. Color changes of the receptor 1 in DMSO/H_2O (9/1) (5.0×10^{-4} M) in absence and presence of 10 equiv. of anions (from the left to the right: 1 only, 1 + F^-, 1 + AcO^-, 1 + $H_2PO_4^-$, 1 + Cl^-, 1 + Br^- and 1 + I^-). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

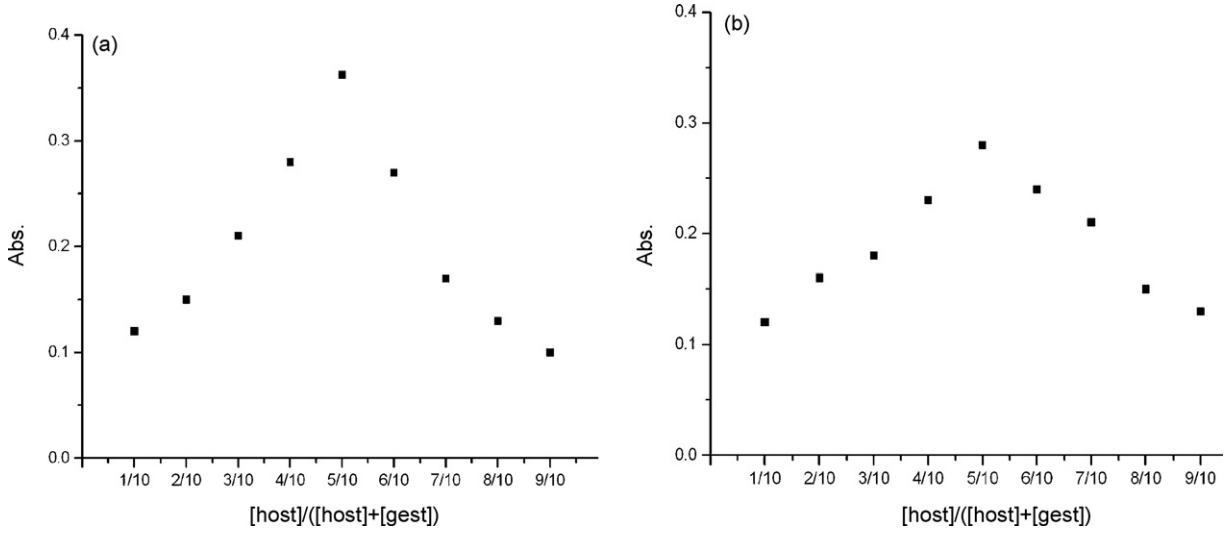


Fig. 4. Job plot for complexation of receptor 1 with F^- (■) determined by UV–vis in (a) DMSO; (b) DMSO/H_2O (9/1) at 298.2 ± 0.1 K, [1] + [anion] = 2.0×10^{-5} M.

one type of host–F^- complex. Similarly, the additions of AcO^- and $H_2PO_4^-$ also led spectral changes. However, as the Cl^-, Br^- and I^- were titrated into 1, the spectra hardly change even the anions added were excessive. The color changes are presented in Fig. 3.

Continuous variation method was used to determine the stoichiometric ratio of the receptor to the fluoride anion guest. In Fig. 4 Job plots [22,23] of receptor 1 and F^- in DMSO and 9/1 DMSO/H_2O show the maxima are all at a molar fraction of 0.5. This result indicates that the receptor 1 binds fluoride anion guest with a 1:1 ratio. Moreover, similar results can also be obtained for other anions (AcO^- and $H_2PO_4^-$).

For a complex of 1:1 stoichiometry, the relation in Eq. (1) could be derived easily, where X is the absorption intensity, and C_H or C_G is the concentration of the host or the anion guest correspondingly [24]:

$$X = \frac{X_0 + (X_{lim} - X_0)\{C_H + C_G + 1/K_{ass} - [(C_H + C_G + 1/K_{ass})^2 - 4C_H C_G]^{1/2}\}}{2C_H} \quad (1)$$

The affinity constants of receptors 1 for the studied anionic species are calculated and listed in Table 1 below.

As a validation to the above qualitative and quantitative analysis, UV–vis changes (Fig. 5) of receptor 1 operated in 9/1 DMSO/H_2O (1.0×10^{-5} M) after the additions of 10 equiv. of anions provided a more convincing evidence that receptor 1 was indeed an excellent sensor for F^-.

Obviously, the recognition function of receptor 1 for F^- is the most remarkable property. The reason may be that receptor 1 has a cavity and it is proper to host F^-, because F^- is spherical geometrically so that can match the receptor better than those trigonal and tetrahedral anions. Further more, F^- is an atomic anion, which means that it can form a five-membered chelate ring with the binding sites that is more stable than seven-membered chelate ring formed by AcO^- or $H_2PO_4^-$. Finally, the ability of F^- binding H^+ is much stronger than Cl^-, Br^- and I^-.

3.2. ^1H NMR titration

To further look into the nature of host–guest interactions, ^1H NMR titration experiments were conducted in DMSO:H_2O (v/v, 9:1) mixtures. ^1H NMR fluoride titration spectra of the sensor 1 is shown in Fig. 6. Upon addition of 0.5 equiv. of fluoride ions, the peaks at 11.51 ppm and 11.61 ppm, which were assigned to aniline –NH and phenole –OH, respectively, were shifted downfield and the signals on the phenyl rings changed slightly. This indicated the formation of a hydrogen-bonding complex was at this stage. With further addition of fluoride ions, upon the addition of 2 equiv. F^-, the signals of –NH and –OH were disappeared and the phenyl protons, espe-

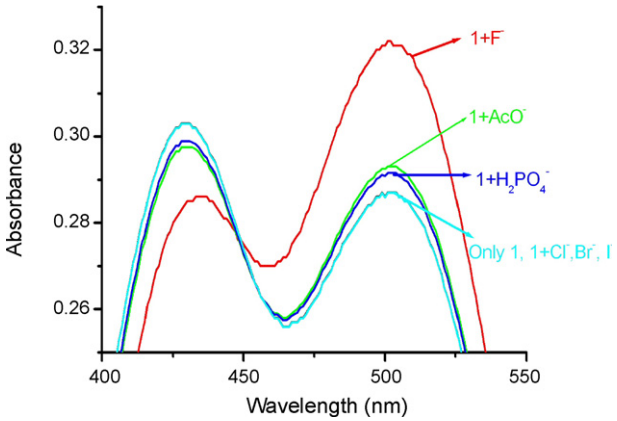


Fig. 5. UV–vis spectra of 1 (1×10^{-5} M) in DMSO/H_2O (9/1) in the presence of 10 equiv. of F^-, or AcO^-, $H_2PO_4^-$, Cl^-, Br^- and I^-.

Table 1
Association constants for various anions toward receptor 1 in DMSO and 9/1 DMSO/H_2O (v/v) at 298.2 ± 0.1 K, respectively.

Anions[a]	F^-	$H_2PO_4^-$	AcO^-	Cl^-	Br^-	I^-
K_{ass} (M^{-1})[b]	$3.71(\pm0.27)\times10^5$	$8.32(\pm0.52)\times10^4$	$1.67(\pm0.13)\times10^5$	ND[c]	ND	ND
K_{ass} (M^{-1})[d]	$8.34(\pm0.57)\times10^3$	$1.03(\pm0.11)\times10^2$	$3.16(\pm0.55)\times10^2$	ND	ND	ND

[a] The anions were added as their tetrabutylammonium salts.
[b] K_{ass} was determined in dry DMSO.
[c] ND indicated that the spectra showed little or no change with the addition of anion so that the association constants cannot be determined using the spectra.
[d] K_{ass} was determined in 9:1 DMSO:H_2O solution.

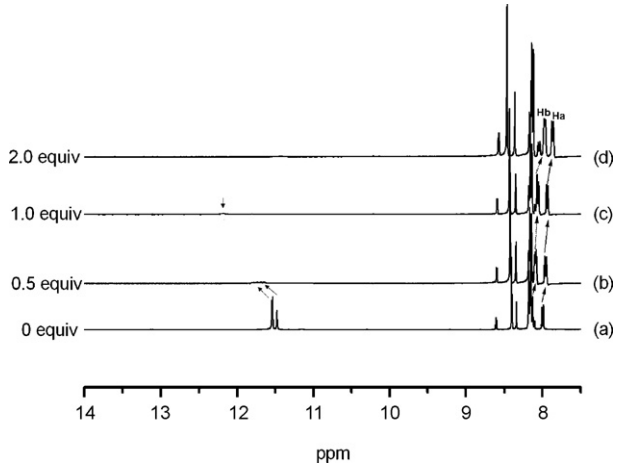
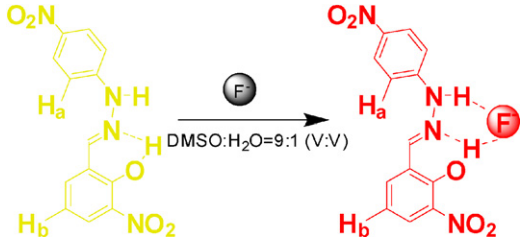


Fig. 6. ^1H NMR titration of a 1×10^{-2} M solution of 1 in DMSO-d_6/H_2O (9/1) with $[Bu_4N]F$.



Scheme 2. The proposed host–guest binding mode in solution.

cially H_a and H_b, moved upfield significantly, which indicated the increase of the electron density on the phenyl ring owing to the through-bond electronic effects. All the results observed indicate that there are two stages during the ^1H NMR titration: (1) in the first stage, the fluoride ion exhibits a hydrogen-bonding interaction with 1, and (2) in the second stage, the excess fluoride ion results the deprotonation of the sensor to take place. Consequently, according to the results of ^1H NMR titration, the proposed binding mode of 1 and F^- was given below in Scheme 2.

4. Conclusion

In summary, we have succeeded in presenting a new kind of colorimetric chemosensor, which showed strong binding affinity as well as a good sensing ability and selectivity for fluoride ion in aqueous (10% water) solution. This outstanding property was bolstered by UV–vis and ^1H NMR titration experiments.

Acknowledgements

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