An acetate sensor based on azo in aqueous media

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ABSTRACT

A colorimetric sensor 1,N,N′-di-(2-hydroxy-5-(phenldiazenyl)benzaldehyde)-1,3-diiminothiourea for acetate in DMSO and 9/1 DMSO/H_2O (v/v) mixtures was designed and synthesized. The binding ability evaluated by UV–vis experiment reveals that sensor **1** can selectively recognize acetate. In addition, the color changes induced by anions can provide a way of detection by 'naked-eye'. The further insights to the nature of interactions between the sensor **1** and AcO$^-$ were investigated by ^{1}H NMR titration experiments in 9/1 DMSO-d_6/H_2O (v/v).

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1. Introduction

Over the past few years, the recognition of inorganic and biotic anions has been a key research area of supramolecular chemistry [1,2] owing to the fundamental role of anions in the environmental and biological systems, and in the clinic practices and so on. For example, the carboxylate anions [3] exhibit specific biochemical functions in the enzymes and antibodies and are also critical components of numerous metabolic processes. Acetate is one of the carboxylate anions with the unique trigonal chemical structure, which can form strong hydrogen-bond interaction with hydrogen-bond donors.

Very recently, the selective recognition of acetate has attracted more and more attention. For example, an effective sensor for acetate ion in dry DMSO was reported by Cheng and co-workers [4]. Ito et al. reported a novel Fipronil-based receptor can selectively recognize acetate among a group of anions in DMSO [5]. We found that the phenylhydrazone-based indole receptor was an effective sensor for acetate ion in dry DMSO [6].

Despite these remarkable achievements, there are still many disadvantages recognized in many examples of literatures. For example, the recognition and/or sensing of anions could only occur in biochemically noncompetitive organic solvents [7,8] (e.g. CH_3CN, CH_2Cl_2, etc.) but unable to sense anions in 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 hopeful to be simultaneously accompanied with 'naked-eyed' detectable color changes [9–11].

By exploiting the optical properties of an azo group, we have recently reported a chromo- and fluorogenic dual responding $H_2PO_4^-$ sensor in dry DMSO [12]. Considering the limited application of this sensor, in this paper, we designed and synthesized a new and simple azo-based receptor (Scheme 1), which is an organic colorimetric chemosensor. The sensing of the biologically important AcO$^-$ is achieved in DMSO solution even in aqueous solution 9/1 DMSO/H_2O (v/v).
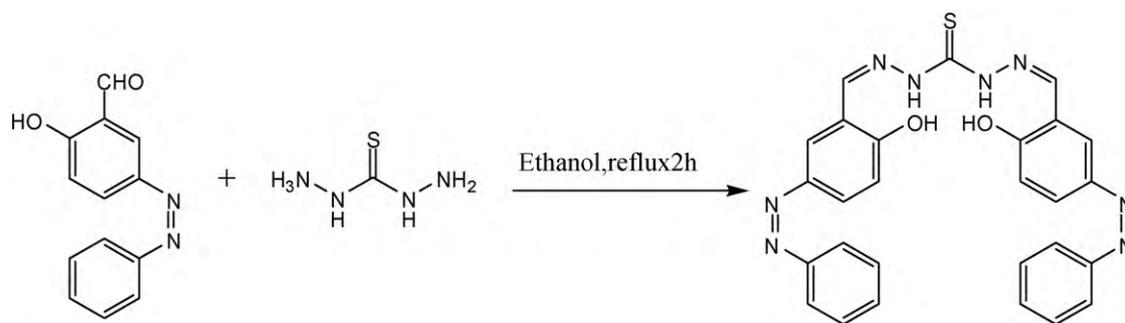
2. Experimental

2.1. Apparatus

^{1}H NMR spectra were obtained on a Varian UNITY Plus-400 MHZ Spectrometer. ESI-MS 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 UV-2450 Spectrophotometer (Shimadzu 2.1 Apparatus Corp., Kyoto, Japan) with a quartz cuvette (path length = 1 cm) at 298.2 ± 0.1 K.

2.2. Reagents

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

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Scheme 1. General synthetic routes to the target sensor **1**.

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 sensor **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 9/1 DMSO-d_6/H$_2$O (v/v) solution (TMS as the internal standard). Certain amount of the sensor **1** solution was prepared with a concentration of 0.01 M. ^{1}H NMR of the host–guest system was recorded by adding increasing amount of acetate into the sensor **1** solution.

2.4. Syntheses and characterization

N,N′-di-(2-hydroxy-5-(phenldiazenyl)benzaldehyde)-1,3-diiminothiourea (**1**)

A solution of 2-hydroxy-5-(phenyldiazenyl)benzaldehyde (0.904 g, 4 mmol) in ethanol (20 ml) was added dropwise to a hot solution of 1,3-diaminothiourea (0.212 g, 2 mmol) in ethanol/water (20 ml, v/v = 1/1) with stirring at reflux. After being stirred for 2 h, the solvent was removed by evaporation after recrystallization from ethanol. This procedure yielded yellow crystals 0.970 g (87%). δ_H (400 MHz, DMSO-d_6, Me$_4$Si): 12.26 (s, 2H, O–H), 12.23 (s, 2H, N–H), 7.87 (dd, 3H, Ar–H), 7.61 (s, 1H, N=C–H), 7.52 (dd, 3H, Ar–H). Elemental analysis: Calc. for C$_{27}$H$_{22}$N$_8$O$_2$S: C, 62.04%; H, 4.24%; N, 21.44%; Found: C, 62.13%; H, 4.02%; N, 21.37%. ESI-mass: m/z 523.58 (M+H)$^+$.

3. Results and discussion

3.1. UV–vis spectroscopy

Firstly, to evaluate the affinity ability to anions, the UV–vis titration experiments of the sensor **1** were carried out in dry DMSO solution using standard tetrabutylammonium salts of AcO$^-$, F$^-$, H$_2$PO$_4^-$, 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 AcO$^-$ is shown in Fig. 1. Upon the addition of AcO$^-$, the broad absorption peaks at 338 nm was decreasing, whereas an absorption peak at 423 nm formed. The resulting titration revealed an isosbestic point at 390 nm.

Secondly, to explore more about the applicability of the sensor **1** for acetate in minor-water-containing solution, the UV–vis titrations were performed in the 9/1 DMSO/H$_2$O (v/v) mixtures. Fig. 2 shows the UV–vis spectral changes of **1** during the titration with acetate. The original absorbance peaks appeared at the
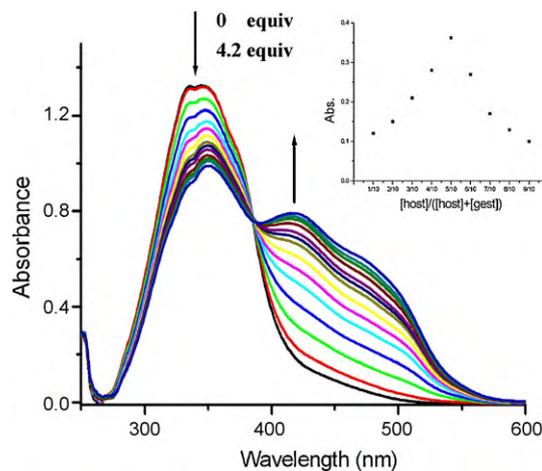

Fig. 1. UV–vis spectrum changes of sensor **1** (2.0×10^{-5} M) upon addition of acetate ion (0–4.2 equiv.) in DMSO at 298.2 ± 0.1 K. Inset: Job's plot for complexation of sensor **1** with AcO$^-$ in DMSO [host] + [guest] = 2.0×10^{-5} M.

λ_{max} of 340 nm, i.e. the π–π^* transition bands of the chromophore (azophenyl). With the addition of more and more doses of acetate ions, the peak at 338 nm decreased but a new peak appeared at 435 nm, which was ascribed to the charge transfer (CT) between the anion-bound –NH and –OH units and the electron-deficient effect from azophenyl. And the color of the sensor **1** solution changed from light yellow to heavy yellow at the same time (Fig. 3). Obviously, there was only one well-defined isosbestic points at 380 nm, which indicated that there existed sole type of **1**–AcO$^-$ complex. Similarly, the additions of F$^-$ and H$_2$PO$_4^-$ also led spectral changes.

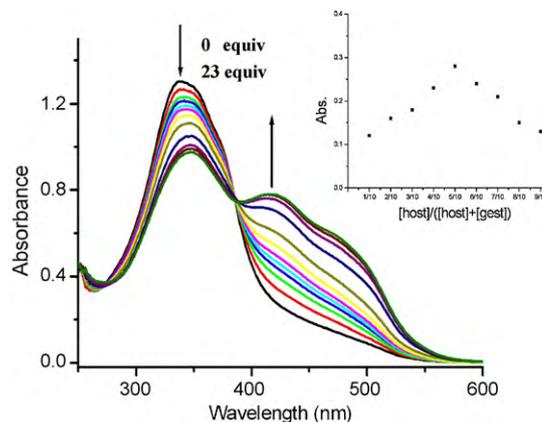**Fig. 2.** UV–vis spectrum changes of sensor **1** (2.0×10^{-5} M) upon addition of acetate ion (0–23 equiv.) in 9/1 DMSO/H$_2$O (v/v) at 298.2 ± 0.1 K. Inset: Job's plot for complexation of sensor **1** with AcO$^-$ in 9/1 DMSO/H$_2$O (v/v) [host] + [guest] = 2.0×10^{-5} M.

Fig. 3. Color changes of the sensor **1** in 9/1 DMSO/H$_2$O (v/v) in absence and presence of anions (from the left to right: **1** only, **1** + AcO$^-$, **1** + F$^-$, **1** + H$_2$PO$_4$$^-$, **1** + Cl$^-$, **1** + Br$^-$ and **1** + I$^-$).

Table 1
Association constants for various anions toward receptor **1** in DMSO and 9/1 DMSO/H$_2$O (v/v) at 298.2 ± 0.1 K, respectively.

Anions[a]	AcO$^-$	H$_2$PO$_4$$^-$	F$^-$	Cl$^-$	Br$^-$	I$^-$
K_{ass} (M^{-1})[b]	3.14(±0.12) × 10^5	7.14(±0.53) × 10^4	7.57(±0.62) × 10^4	ND[c]	ND	ND
K_{ass} (M^{-1})[d]	7.37(±0.54) × 10^3	1.62(±0.19) × 10^2	2.73(±0.24) × 10^2	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 9/1DMSO/H$_2$O (v/v)solution.

However, as adding Cl$^-$, Br$^-$ and I$^-$ to **1**, the spectra responses are not obvious.

Continuous variation method was used to determine the stoichiometric ratio of the receptor to the fluoride anion guest. Job's plot [13,14] of sensor **1** and AcO$^-$ in DMSO and 9/1 DMSO/H$_2$O (v/v) (Figs. 1 and 2) shows the maxima are all at a molar fraction of 0.5. This result indicates that the sensor **1** binds acetate anion guest with a 1:1 ratio. Moreover, similar results can also be obtained for other anions (F$^-$ and H$_2$PO$_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 [15].

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

(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. 4) of sensor **1** operated in 9/1 DMSO/H$_2$O (v/v) (2.0 × 10^{-5} M) after the additions of 17 equiv. of anions provided a more convincing evidence that sensor **1** was indeed an excellent sensor for AcO$^-$.
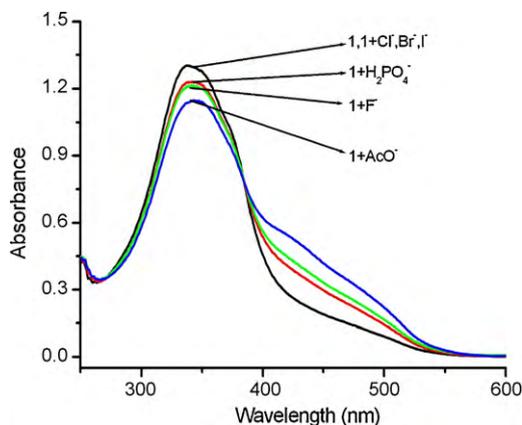
As clearly shown in Table 1, the order of binding affinity of **1** with anions (in DMSO or DMSO/water) is AcO$^-$ » F$^-$ > H$_2$PO$_4$$^-$ ~ Cl$^-$ ~ Br$^-$ ~ I$^-$. The recognition function of sensor **1** for AcO$^-$ is the most remarkable property. The main reason for preferring AcO$^-$ is its triangular shape which determines the angle of O–C–O is about 120° while the angle of O–P–O in H$_2$PO$_4$$^-$ is about 108°. The distance of two oxygen atoms of AcO$^-$ might be more fit to the hydrogen atoms of the recognition sites than those spherical and tetrahedral anions. That is, the configuration of AcO$^-$ is more matching with **1** than F$^-$ and H$_2$PO$_4$$^-$.

Compared with the previous research in our laboratory [12], the sensor **1** has higher selectivity for acetate than receptor **1**, because the structure of sensor **1** is symmetrical while receptor **1** is unsymmetrical in the lecture [12]. The advantage of configuration made sensor **1** has better selectivity than receptor **1**. So the association constant of sensor **1** with AcO$^-$ is much bigger than receptor **1** in the lecture.

3.2. ^{1}H NMR titration

To further look into the nature of host–guest interactions, ^{1}H NMR titration experiments were conducted in 9/1 DMSO-d_6/H$_2$O (v/v) mixtures. ^{1}H NMR acetate titration spectra of the sensor **1** is shown in Fig. 5. Upon addition of 0.5 equiv. of acetate ions, the peaks at 12.23 ppm and 12.26 ppm, which were
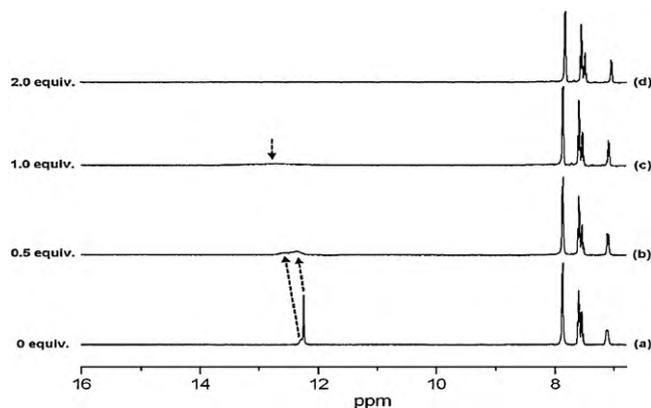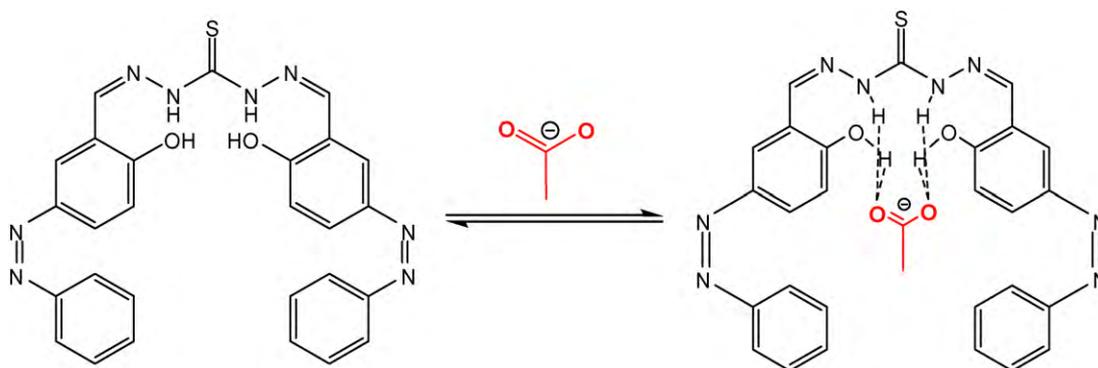

Fig. 4. UV–vis spectra spectra of **1** (1 × 10^{-5} M) in 9/1 DMSO/H$_2$O (v/v) in the presence of 17 equiv. of F$^-$, or AcO$^-$, H$_2$PO$_4$$^-$, Cl$^-$, Br$^-$ and I$^-$.

Fig. 5. ^{1}H NMR titration of a 1 × 10^{-2} M solution of 1 in 9/1 DMSO-d_6/H$_2$O (v/v) with [Bu$_4$N]AcO.

Scheme 2. The proposed **1**–AcO⁻ binding mode in solution.

assigned to aniline–NH and phenole–OH, respectively, were shifted downfield to 12.43 ppm and 12.57 ppm 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 acetate ions, upon the addition of 2 equiv. AcO⁻, the signals of –NH and –OH were disappeared and the phenyl protons 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 acetate ion exhibits a hydrogen-bonding interaction with **1**, and (2) in the second stage, the excess acetate 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 AcO⁻ 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 selectivity for acetate ion in aqueous solution. This outstanding property was bolstered by UV–vis and ¹H NMR titration experiments. It is expected to be applied for detection of acetate in real life for its easy synthesis and highly selectivity.

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