



A novel colorimetric receptor responding AcO^- anions based on an azo derivative in DMSO and DMSO/water solution

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ABSTRACT

A novel and efficient receptor based on the phenylhydrazone derivatives is successfully developed and applied to the acetate anion recognition, indicating that the origin of special preference for acetate (AcO^-) anion maybe the structure well matching between the host and the guest. The sensor changes its color so obviously on addition of the acetate ions and that may make the naked-eye recognition in DMSO and even in DMSO/ H_2O (95/5) solution come true. Also, the anion binding ability determinations were performed by UV–vis titration and ^1H NMR titration experiments with different anions in the solutions mentioned. The fluorescence enhancement can also be observed after the host is coordinated with the AcO^- anion and excited by light wavelength at 280 nm.

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1. Introduction

Because of anions' crucial role in the biological fields, medical systems and environmental science, a great deal of work has been focused on the design and synthesis of the selective receptors for anions in the past two decades. As a result, anion recognition has been developed into a fastest growing branch of supramolecular chemistry [1,2]. Accordingly, how to effectively recognize and sense anions through the naked eye, electrochemistry and/or fluorescent responses have attracted considerable attention [3–5]. Generally speaking, colorimetric and/or fluorescent chemosensors are made up of two main fragments, which involve the binding sites that interact with anions either electrostatically or through hydrogen bonding, etc., and the signal parts that connect to the binding sites either directly or intramolecularly linked which show the color changes, fluorescence quenching or enhancing, etc. [6–9] in the anion recognition procession. With regard to the binding sites, the functional groups such as amine [10], urea [11] and hydroxyl groups [12] are numerous used owing to their capacity to perform as hydrogen donors. Otherwise, if taking advantage of the electrostatic interaction, the quarterized nitrogen [13] and positively charged pyridine [14] may be firstly chosen as binding sites. However, among the colorimetric and

fluorescent parts of the receptors for the anion sensing, simplicity and high selectivity [15,16] are still challenges for investigators and they attract much interests. In particular, to develop the naked-eye detection technique for the analytic without using any expensive equipment is of great interest in recent years. Azo as the optical group has already been reported as the functional group of the sensor molecules in the literature [17,18].

Among the various types of anions, carboxylate anion is one of the biochemically important anions because it exhibits vital behaviors in the enzymes and antibodies and is also the significant component of numerous metabolic processes [19]. Therefore, to recognize and sense the acetate ions is thought to be more and more important than other biologically functional anions. Nie et al. [20] have shown that phenylthioureas based on substituted benzamido were better to bind to acetate than to other anions in acetonitrile. Besides, we [21] reported *di*-nitrocabazole could also be the efficient receptors for acetate. Unfortunately, there are still shortcomings with the whole literature on sensing anions, e.g., the studies reported were restricted as they can be conducted only in the noncompetitive organic solvents [22,23], because the competitive protic solvent interacts with the anion by H-binding prior to the host with the anion. So the recognition of acetate anions in aqueous solution is still a challenging work.

In this paper, we designed and synthesized a new and simple anion receptor that contained both hydrogen-bond-donor group (phenylhydrazone) and colorimetric group (azo). Its anion

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recognition behaviors and sensitivity to biologically important fluoride, acetate and phosphate, but high selectivity to acetate anion according affinity constants than other anions, were studied in dry DMSO and in aqueous solution. And the recognition is found by forming the hydrogen bonding at charge-neutral sites. In addition, the sensing processes can be realized by the 'naked-eye' determination as it has a remarkable color response.

2. Experimental

2.1. Materials

All reagents for synthesis obtained commercially were used without further purification. In the titration experiments, all 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.

2.2. Apparatus

^1H NMR spectra were obtained on a Varian UNITY Plus-400 MHz Spectrometer. ESI-MS was performed with a MARINER apparatus. C, H, N elemental analyses were made on an Elementar vanio EL. UV-vis spectra were recorded on a Shimadzu UV-2450 Spectrophotometer with a quartz cuvette (path length=1 cm) and fluorescent spectra were recorded on a Shimadzu RF-5301PC Spectrophotometer at 298.2 ± 0.1 K and the width of the slits used was 10 nm; ESI-MS was performed with a MARINER apparatus.

2.3. General procedure

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 5.0×10^{-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^{-3} M tetrabutylammonium salts of the respective anions were prepared in the dried and distilled DMSO and were stored under a dry atmosphere.

^1H NMR titration experiments were carried out in the $\text{DMSO}-d_6$ solution (TMS as an internal standard). A 0.01 M solution of the compound 1 in the $\text{DMSO}-d_6$ was prepared. Then, the additional amount of acetate anion (1.0 M in $\text{DMSO}-d_6$) was added to the

solution mentioned above and ^1H NMR of the host-guest system was tested.

2.4. Synthesis

2.4.1. 5-Phenylazo-salicylaldehyde

The synthesis route of compounds 1 and 2 is demonstrated in Scheme 1. 5-Phenylazo-salicylaldehyde was prepared according to Ref. [24]. To a solution of 5 ml aniline (0.05 mol) in a small quantity of water was added slowly 6 ml of 37% HCl at $0-5^\circ\text{C}$ when stirring. Then, 20 ml of 20% NaNO_2 was added to the above-mentioned mixture and the resulting solution was stirred for 1 h to give a bright yellow solution. Five milliliters of salicylaldehyde (0.05 mol) was dissolved in the solution of NaCO_3 ($18\text{ g NaCO}_3 + 150\text{ ml H}_2\text{O}$). Then the solution of salicylaldehyde was added dropwise to the bright yellow solution for 1 h. After stirring for 4 h, the reaction mixture was neutralized with HCl. The brown crude solid was filtered and recrystallized from ethanol to afford a pure product. Mp: 120°C .

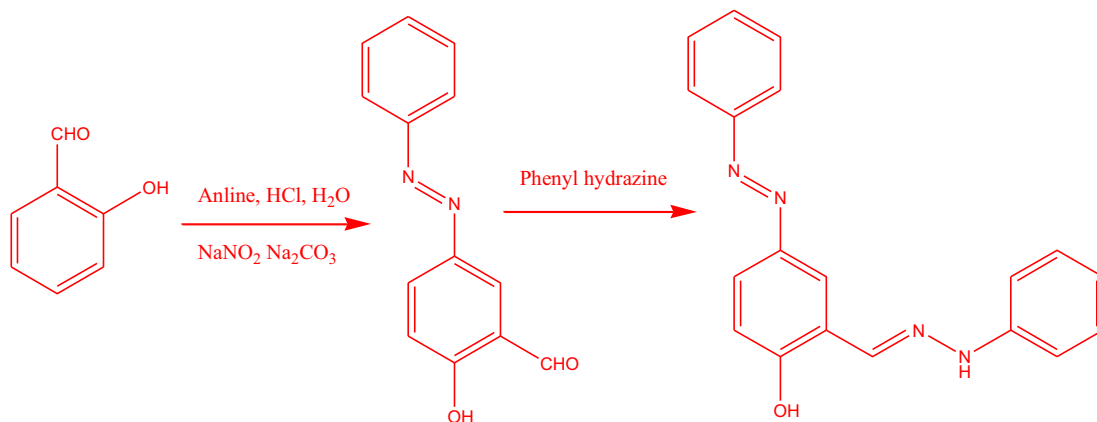
2.4.2. 4-Phenylazo-2-hydroxy-benzaldehyde phenylhydrazone

For 2.26 g (10 mmol) 4-phenylazo-2-hydroxy-benzaldehyde, 1.08 g (10 mmol) phenyl hydrazine and four drops of acetic acid were dissolved in 100 ml $\text{CH}_3\text{CH}_2\text{OH}$ and then the resulting solution was heated and refluxed for 2 h. The mixture solution was cooled at room temperature after reaction. The precipitate formed was filtered, and 2.69 g pure yellow solid was obtained after recrystallization by $\text{CH}_3\text{CH}_2\text{OH}$. Yield=85%. ^1H NMR ($\text{DMSO}-d_6$): δ 11.14 (s, 1H, OH H₁), 10.54 (s, 1H, NH H₂), 8.24 (d, 2H, phenyl), 7.88 (d, 2H, phenyl), 7.76 (d, 1H, phenyl), 7.57 (t, 3H, phenyl), 7.26 (d, 2H, phenyl), 7.04 (t, 3H, phenyl), 6.79 (s, 1H Ha); ESI-mass: $m/z=315.07$ [M]⁻; element analysis calcd for $\text{C}_{19}\text{H}_{16}\text{N}_4\text{O} \cdot \text{CH}_3\text{CH}_2\text{OH}$: C, 72.13; H, 5.10; N, 17.71. Found: C, 72.10; H, 5.09; N, 17.71.

3. Results and discussion

3.1. UV-vis spectral titrations

The anion binding properties of the synthesized receptor 1 were investigated by UV-vis titrations at room temperature in DMSO solution. Various anions were taken in the form of the tetrabutylammonium (TBA) salts. Fig. 1 shows the significant UV-vis spectral changes of sensor 1 on addition of acetate ion. As we gradually added the AcO^- into the solution (2×10^{-5} M), the absorbance band centered at 353 nm, ascribed to the charge-



Scheme 1. Synthesis of sensor 1

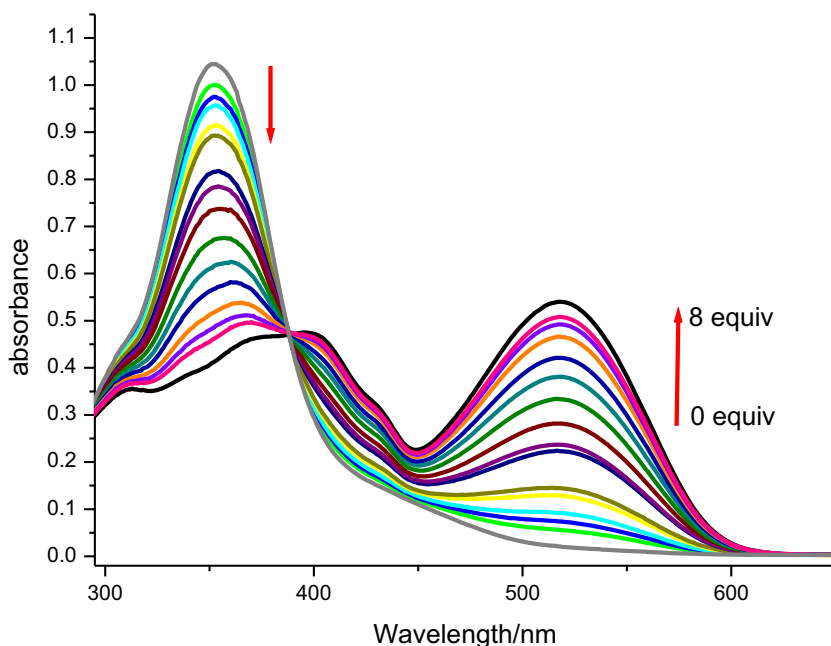


Fig. 1. Changes in the absorption spectra of 1 (2×10^{-5}) on addition of AcO^- in DMSO.

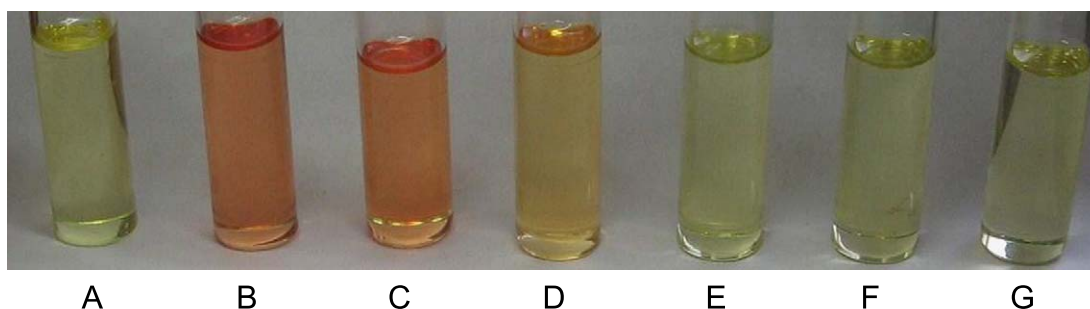


Fig. 2. Color changes of sensor 1 in DMSO (2×10^{-5} mol L $^{-1}$) after addition of 10 equiv. anions. A: 1 only; B: 1+ AcO^- ; C: 1+ F^- ; D: 1+ H_2PO_4^- ; E: 1+ Cl^- ; F: 1+ Br^- ; G: 1+ I^- .

transfer of the phenyl hydrazine [25], diminished little by little accompanied with a new band generated at 518 nm, suggesting the formation of the complex between receptor 1 and acetate ion. The color change from light yellow to red could be easily detected by the naked eye (see Fig. 2). As shown from Fig. 1, there was a well-defined isosbestic point at 390 nm, which indicated the presence of only one type of host– AcO^- complex. Moreover, addition of anions of F^- and H_2PO_4^- in the solution induced UV–vis spectral changes and color responses obtained with addition of AcO^- . On the contrary, addition of excess amount of halide anions of chloride, bromide and iodide into the solution did not result in any visible spectrum responses (Fig. 3).

Generally, the protic solvent such as methanol and water would compete with the binding parts of the hosts for anions and, thus, could disturb the interaction between the receptor and the anions. To our surprise, however, notable color changes were observed with increase in concentration of AcO^- , F^- and H_2PO_4^- from light yellow to red in DMSO/ H_2O (95/5) solution. Furthermore, the UV–vis titrations were also investigated in DMSO/ H_2O (95/5) mixtures (Fig. 4), where sensor 1 revealed a strong band at 352 nm, and similar spectral changes as in the dry DMSO solution on addition of AcO^- (see Fig. 4). Likewise,

on addition of AcO^- , the bands centered at 518 nm were gradually enhanced and a well-defined isosbestic at 390 nm appeared, and this was accompanied with color changes from light yellow to red suggesting that the receptor 1 can act as a sensitive and visible colorimetric sensor. Among the types of anions tested, the similar spectral changes with AcO^- were happening only to the F^- and H_2PO_4^- anions but not to the Cl^- , Br^- and I^- anions. Thus, the concept of the anion sensing and binding affinity of the anions for receptor 1 was through hydrogen bonds alone which could not be inferred by the test done in the solvent of adding the 5% water in the DMSO. Two main reasons might rationalize the requirement of new thoughts. One fact is that the DMSO is a solvent with very good hydrogen-binding affinity and it can strongly interact with the water molecules in the concentration utilized. The other is that the NH group has been proved to be better hydrogen-bonding donor, however, it can strongly bond with the water molecules as well in the concentration utilized [26]. Recently, Han et al. [27] have reported the behavior of thiourea-based receptors in the less protic 3% MeOH solution and their saturated spectroscopic absorptions could hardly be obtained until adding 1000 eq. F^- ion. Consequently, the receptor 1

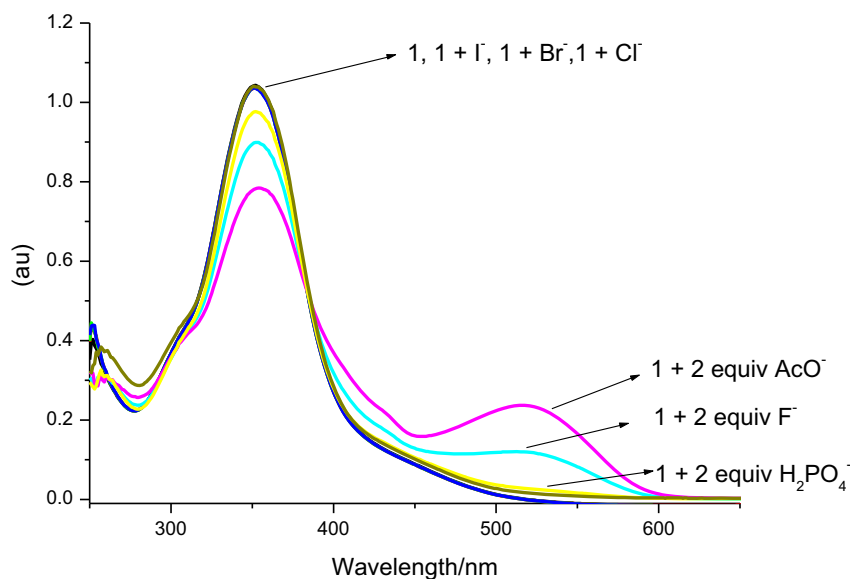


Fig. 3. UV-vis spectra of **1** (2×10^{-5} M) in [95:5] DMSO/H₂O (95/5, v/v) in the presence of 2 equiv. of AcO[−] ion and miscellaneous anions including F[−], H₂PO₄[−], Cl[−], Br[−] and I[−].

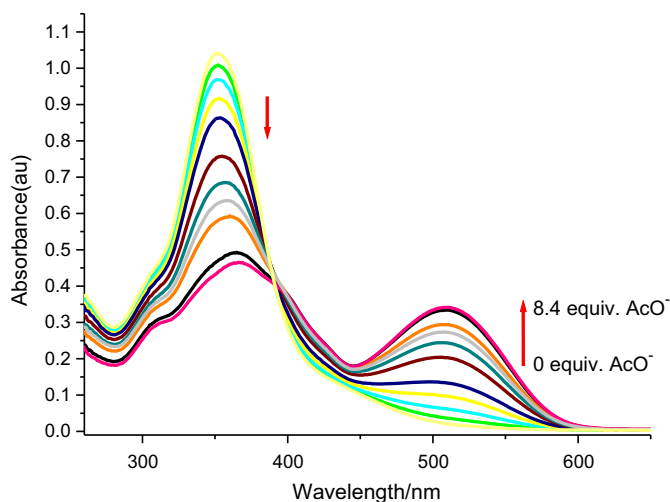


Fig. 4. Titration of 2×10^{-5} mol l^{−1} solution of **1** with a standard solution of tetrabutylammonium acetate anion in [95/5] DMSO/H₂O (95/5, v:v)

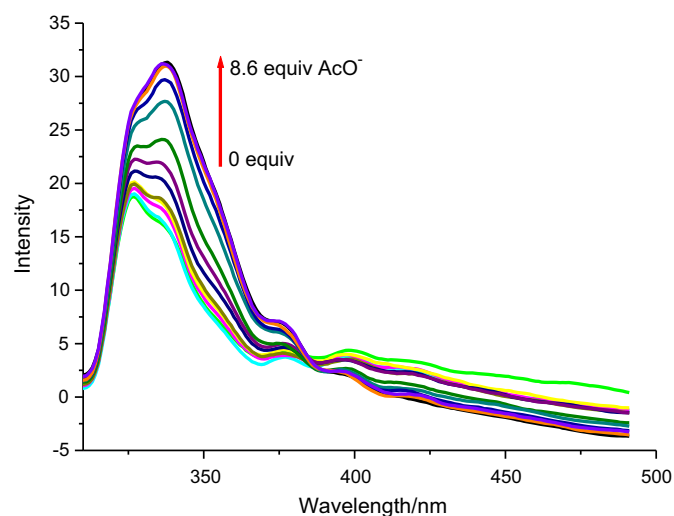


Fig. 5. Fluorescent changes of sensor **1** in DMSO (2×10^{-5} M) on addition of AcO[−] ions

could be a more effective colorimetric sensor for anions recognition in the aqueous solution which may shed light on a new thought that the well matched geometries between host and guest may be a better improvement for the host interacting with the guest.

3.2. Fluorescent responses of receptor **1** toward anions

The interactions of the anions with receptor **1** were determined by the fluorescent spectroscopic titrations in DMSO solution. The fluorescence responses of the host adding the anions were observed on exciting at 280 nm and the changes were recorded in Fig. 5. As shown in Fig. 5, the free receptor **1** (2×10^{-5} M) in DMSO has the main emission band centered at 330 nm. On adding the AcO[−] anion, the solution gave rise to a dramatic enhancement in fluorescence intensity at this emission band. Two possible mechanisms may be given in

interpretations of the fluorescent enhancement: (1) inhibition of photoinduced electronic transfer (PET) [28] and (2) the guest binding-induced rigidity of the host molecule [29,30]. Without adding the AcO[−], the nitrogen atoms of the free receptor **1** could form an intramolecular hydrogen bond with the hydrogen atom of the hydroxyl group, which led to a photoinduced electron transfer and the fluorescence was thus weakened. However, on addition of the acetate to the solution, the binding sites of the host interacted with the guest forming the host–anion complex that resulted in the PET inhibition and intensity of the fluorescent spectrum increases. In addition, before coordination of receptor **1** with AcO[−] anion, the configuration of the receptor was uncontrolled and it could be flexibly and freely rotated. While the fluorescence could be increased by the coordination of receptor **1** with acetate anions, inhibiting vibrational and rotational relaxation modes of nonradiative decay gave rise to the fluorescent enhancement. Meanwhile, addition of F[−] and H₂PO₄[−] ions led to similar

fluorescent responses with respect 1 as the AcO^- did but sensor 1 was insensitive to the addition of Cl^- , Br^- and I^- ions even when excess amount is added. Accordingly, the titration of the anions in the mixture solution DMSO/ H_2O (95/5) gave rise to a

similar change in the DMSO solution (see Supporting information Fig. 9).

3.3. Determination of affinity constants

As shown by the titration curves in Fig. 6, they all fitted satisfactorily to a 1:1 binding mode as proved by the non-linear fitting analyses (particular, as for acetate anion see Fig. 6), and determined by the non-linear fitting analyses. The affinities of the anions for receptor 1 (in DMSO or DMSO/ H_2O in 95/5) followed the order $\text{AcO}^- > \text{F}^- > \text{H}_2\text{PO}_4^- \gg \text{Cl}^- \sim \text{Br}^- \sim \text{I}^-$ (Table 1). Although a full understanding of the principles that govern anion recognition has not yet been achieved, it already becomes clear early on that the selectivity for special anions can be rationalized on the basis of guest basicity and shape complementarity between host and anionic guests [31]. Actually, it is necessary that the sensor possesses the multiple hydrogen-bonding interaction offering the high-affinity anion binding sites. In particular, the best selective recognition for AcO^- ions was most likely due to its best complementarity between the acetate anion and receptor 1 among the anions tested. It is quite clear that the acetate anion is a planar and triangular species and the angle $\text{O}-\text{C}-\text{O}$ is about 120° , which fits very well to the two hydrogen atoms of the recognition site of the sensor. So the acetate anions interacted with receptor 1 and formed effective multiple hydrogen bindings (see Scheme 2). On the other hand, by the alkalinescence of the acetate anion and the basicity of the receptor,

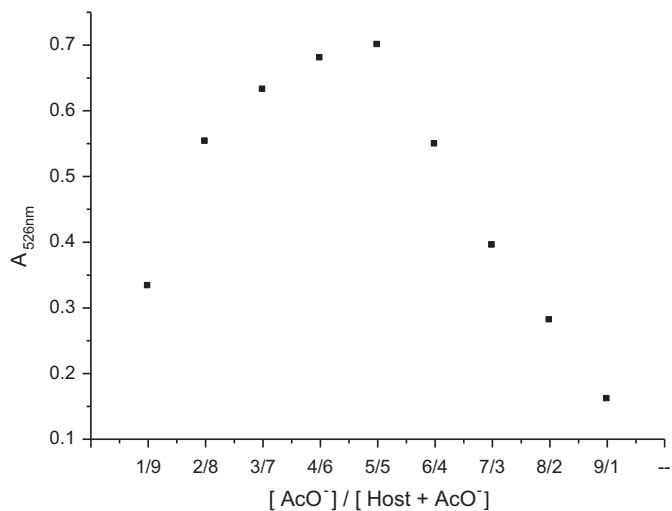


Fig. 6. The stoichiometry analysis of complex formation [1. AcO^-] by Job plot analysis: $[1] + [\text{AcO}^-] = 10 \times 10^{-5} \text{ mol l}^{-1}$ at $298 \text{ K} \pm 0.1 \text{ K}$

Table 1

Association constants (K_{ass} , M^{-1}) of sensor 1 with anions in DMSO and DMSO/ H_2O (95/5, v/v) at $298.2 \pm 0.1 \text{ K}$.

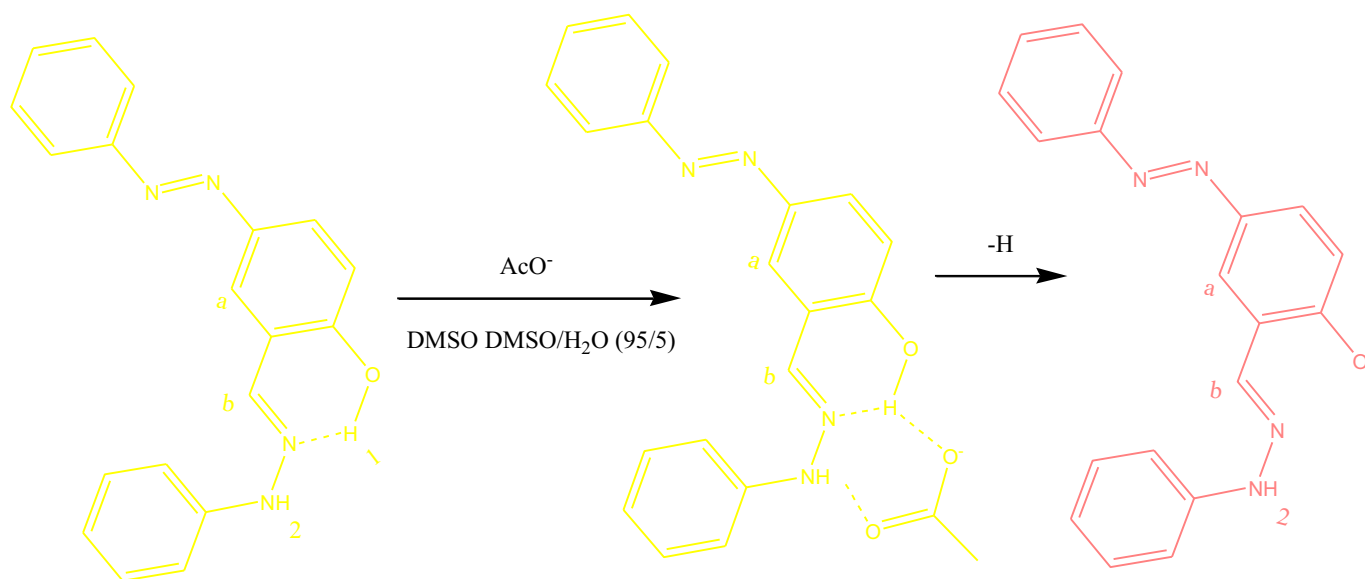
| Anions ^a | F^- | AcO^- | H_2PO_4^- | Cl^- | Br^- | I^- |
|-----------------------------|-----------------------------|-----------------------------|-------------------------------|-----------------|---------------|--------------|
| $K_{\text{ass}}^{\text{b}}$ | $2.60 \pm 0.25 \times 10^3$ | $8.04 \pm 0.42 \times 10^3$ | $2.17 \pm 0.81 \times 10^3$ | ND ^c | ND | ND |
| $K_{\text{ass}}^{\text{d}}$ | $2.19 \pm 0.80 \times 10^3$ | $4.33 \pm 0.73 \times 10^3$ | $0.455 \pm 0.082 \times 10^3$ | ND | ND | ND |

^a All anions were added in the form of tetra-*n*-butylammonium (TBA) salts.

^b Association constant was determined in DMSO.

^c ND the spectra change very little with addition of anion and hence this is not of use to determine the affinity constant by the spectra.

^d The association constant was determined in DMSO/ H_2O (95/5).



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

we see that the acetate should not fit better than those more basic F^- and $H_2PO_4^-$ anions. But as for F^- , its small ball shape could not match the binding site properly and the tetrahedral shape of dihydrophosphate anion should also fit the binding site of the sensor worse than AcO^- to form the multiple hydrogen bonds. Then, because the alkalinescence of the Cl^- , Br^- and I^- was weaker than of the acetate anions, the acetate anions should be the one most highly selected by receptor 1.

3.4. 1H NMR titrations

1H NMR titration was conducted to further investigate the nature of the receptor–anion interactions. The tetrabutylammonium acetate ions were dissolved in $DMSO-d_6$ because of the limited solubility of 1 in $DMSO/H_2O$ (95:5) mixtures, and the series of 1H NMR spectral titration curves of the receptor 1 (1×10^{-2} M) were recorded in Fig. 7. As we see from Fig. 7, the peak at 11.14 ppm, assigned to OH group, broadened and finally disappeared we keep adding acetate anions to 2.0 equiv. The outcome showed that the proton of the hydroxyl group was completely deprotonated due to addition of the acetate ion. Simultaneously, the peak at 10.54 ppm, ascribed to hydrazone N–H protons, shifted upfields (from 10.54 to 9.85 ppm) and the phenyl ring protons (H_a , H_b), especially for H_b , also moved upfields significantly, indicating the electron density on the phenyl ring increased on increasing the concentration of the acetate to 0.8 equiv. These changes clearly indicate that the sensor–anion interaction indeed involved the formation of hydrogen-bond (Scheme 2). Accordingly, two effects [32] could be adopted to rationalize the spectral changes of the aromatic proton, on NH and anion interacting via H-binding: (1) deshielding effect, i.e. a downfield shift is induced by the space effect which polarizes the C–H bond in proximity to the hydrogen bond and produces the partial positive change on the proton and (2) shielding effect which resulted from the electron density increase of the phenyl rings through the bond spreading. The proton of hydroxyl group is induced, through the deprotonation by adding AcO^- anions, and hence the electron density diffuses to the phenyl ring through bonding and brings the protons of H_a and H_b shift upfield. Consequently, all the results imply that anion recognition underwent two steps: the acetate anion induced the proton of

the hydroxyl group deprotonated, and then, the hydrazones N–H interacted with anions through hydrogen binding forming complex. The titration of OH^- anion demonstrates the proposed coordination mechanism (Fig. 8). As a result, the spectrum of the 1H NMR titration testified that the interaction between the anion and the host was very efficient.

4. Conclusion

In summary, a simple colorimetric receptor was successfully synthesized in high yields and here azo was treated as a signaling unit and phenylhydrazone acted as the binding sites. The anion recognition properties via hydrogen-binding interactions were investigated by UV–vis and 1H NMR titrations and the spectrum could be easily changed on addition of anions. Meanwhile, the unique color change was observed from light yellow to red on addition of AcO^- , F^- and $H_2PO_4^-$ ions in $DMSO$ and $DMSO/H_2O$ (95/5) solution. Meanwhile, although the aqueous solution could exclude the interference from $H_2PO_4^-$ and improve the selectivity for AcO^- , it shows little effect relevant to F^- anion sensing. Therefore, the receptor has a potential of application to detect acetate anion in real life and we are exploring the sensing ability of framework related to receptor 1 that could detect anions in more water solution.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jlum.2009.10.015.

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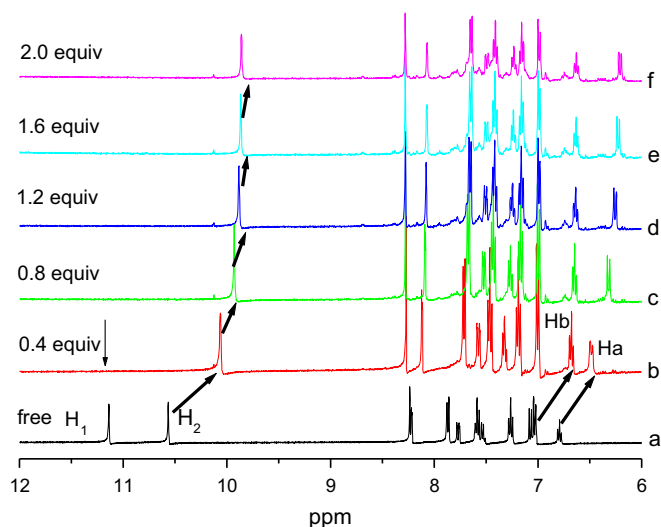


Fig. 7. 1H NMR spectra of receptor 1 in $DMSO-d_6$ (1×10^{-2}) on addition of molar equiv. of AcO^- .

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