Colorimetric Sensing of Biologically Important Acetate Ion Based on Indole Derivation

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Abstract: A simple and novel receptor 1 based on indole-3-aldehyde and 2, 4-diphenylhydrazine is synthesized by a simple way, which displays good selectively and sensitivity for detection of acetate, fluoride and dihydregen phosphate anion in dry DMSO and in DMSO/H_2O (95/5) solutions. Combining with the anions induces the visible color changes that the naked-eye detection maybe realized. Meanwhile, the binding properties are tested and determined by UV-vis, fluorescent changes and ^1H NMR experiments in DMSO-d_6.

Keywords: Indole, Phenylhydrazone, anion recognition, Naked-eye recognization.

1. INTRODUCTION

Recently, anion recognition and sensing have attracted considerable attention for the crucial roles of the anions in industrial, environmental and biological [1,2] fields. Among them, acetate, fluoride and dihydrogen phosphate anion are of great concern for their purposes in the chemistry of enzymes and antibodies; in the treatment of osteoporosis and the prevention of dental caries, and in the energy storage in biological systems, respectively [3-5]. Because of such a diversity of their usages, it is necessary to develop sensitive and selective methods that can detect these kinds of anions without resorting to any expensive spectroscopic instrumentation. Consequently, colorimetric anion sensors [6,7] is more and more appealed by the researchers, especially considering the colorimetric anion sensing system may allow a simple convenient way for the anion detection, i.e. the so-called 'naked-eye' detection. One of the successful strategies used for the preparation anionic sensors is to design and synthesize the chemosensors containing the optical-signaling chromophoric moieties linked to the functional group with covalent or noncovalent bonds. And they interact with the anions through intermolecular hydrogen bond, electrostatical interaction and so on [8-11]. In general, a range of functional group containing N-H hydrogen-bond donors is employed, for example amide [12], urea [13], thiourea [14], phenol [15], or pyrrole subunits [16] and so on.

Inspite of the large variety of hydrogen-bond donor systems that have investigated in this field, little attention has been paid to indole (biindole) as an anion receptor moiety for this purpose. Recently, the indole has also been demonstrated to be H-bond donors to selectively and strongly coordinate the anion [17]. Moreover, Sessler and co-workers [18], Jeong and co-workers [19], and Beer [20] have also revealed that the indole and biindole sensors show high affinities and selectivity to anions such as acetate, dihydrogen phosphate or fluoride. Although having the obvious achievements, there are still lots of disadvantages appearing in a series of elegant literatures. For instances, the sensing or/and recognition of anions mostly occurred in the noncompetitive organic solvents [15, 21-23] but not in the competitive protic solvents as water, ethanol and so on. Considering the latter solvents are widely encountered, as s result, it is necessary to develop sensors capable of binding anions within these competitive media and of detecting anions by the 'naked-eye' sensing of the color changes [24]. Based on this, we have discovered that indole-dione phenylhydrazone compounds have high affinities for oxoanions and selectivity for acetate anion in DMSO solution [10].

Facing this situation, we designed and synthesized anion receptor, i.e. the related indolealdehyde hydrazone (compound 1) containing the indole-3-aldehyde and *2, 4*-dinitrophenylhydrazine. As might be expected, it was sensitive to anions and exhibited a special color change in the presence of F^-, AcO^- and $H_2PO_4^-$ anions. Interestingly, the receptor recognized the biologically important AcO^- anions even in DMSO-water mixtures *via* hydrogen binding. All these results expose that the compound 1 has the high ability to compete with water for anion binding so that the distinguishing feature might be used for practical detection of AcO^- anion in real life. In addition, the interactions between the host and the anions not only induced the absorption spectrum changes, accordingly, it is demonstrated that the sensor can effectively detect AcO^- anion in DMSO and in aqueous solution (DMSO/H_2O 95/5).

2. EXPERIMENT

2.1. Materials

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.

2.2. Apparatus

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

2.3. General Methodology

All experiments were carried out at 298.2 ± 0.1K, 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 salt of the respective anion were

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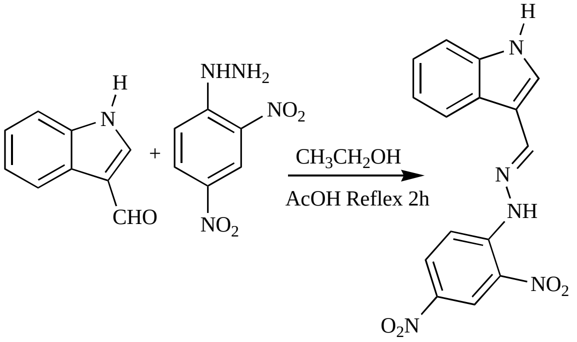
prepared in dried and distilled DMSO and were stored under a dry atmosphere.

^{1}H NMR titration experiments were carried out in the DMSO-d_6 solution (TMS as an internal standard). Certain amount of 0.01 M solution of the compound 1 in the DMSO-d_6 was prepared, into which the increased amount of acetate anion (1.0 M in DMSO-d_6) was added and ^{1}H NMR of the host–guest system was recorded.

2.4. Synthesis of indole-3-aldehyde 2, 4-dinitrophenylhydrazone (Compound 1)

The structures and synthesis of receptor 1 are shown in Scheme **1**. 0.29 g (2 mmol) 3-Indolealdehyde, 0.396 g *2.4*-dinitrophenylhydrazine (2 mmol) and four drops of acetic acid as a catalyzer were dissolved in 40 mL CH_3CH_2OH and then the resulting solution was heated and refluxed for 2 hours. The mixture was cooled at room temperature after reaction. Precipitate formed was filtered, and 0.553 g pure red solid was obtained after recrystallization by CH_3CN. Yeild=85%. ^{1}H NMR (DMSO-d_6, 300 MHz) δH 7.27 (d, 2H, Ar-H, *J* = 2.6 Hz), 7.51 (s. 1H Ar-H), 7.93 (s, 1H, -CH=N), 8.03 (s, 1H, Ar-H), 8.28 (s, 1H, Ar-H), 8.43 (d, 1H, Ar-H), 8.90 (d, 2H, Ar-H, *J* = 9.6 Hz), 11.63 (s, 1H, pyrole-NH H2), 11.84 (s, 1H, =N-NH- H1), Elemental analysis calcd for $C_{15}H_{11}N_5O_4$ (325.3): C: 55.38, H: 3.41, N: 21.53, Found: C: 55.36, H: 3.40, N: 21.51.



Scheme 1. Synthesis of the sensor **1**.

3. RESULTS AND DISCUSSION

The co-ordination properties of the synthesized derivatives reacting with anions were firstly investigated by UV-vis spectroscopic titrations in DMSO solution. Various anions tested, such as F^-, AcO^-, $H_2PO_4^-$, Br^-, Cl^-, and I^-, were taken as tetrabutylammonium (TBA) salts. Fig. (**1**) exhibits the UV–vis absorption spectra of receptor 1 (1.0×10^{-5} M) with various anions, so as to be able to qualitatively estimate the affinity of the sensor. Just as shown the Fig. (**1**), the anions of AcO^-, F^- and $H_2PO_4^-$, especially acetate ions, induce the obviously spectral changes, which were observed instantaneously from light yellow to red (See Fig. **2**) upon addition of 10 equiv of F^-, AcO^- or $H_2PO_4^-$ into DMSO solutions of sensor **1**. On contrary, even addition of large amount of the other tested anions no spectral responses and color changes were led to.

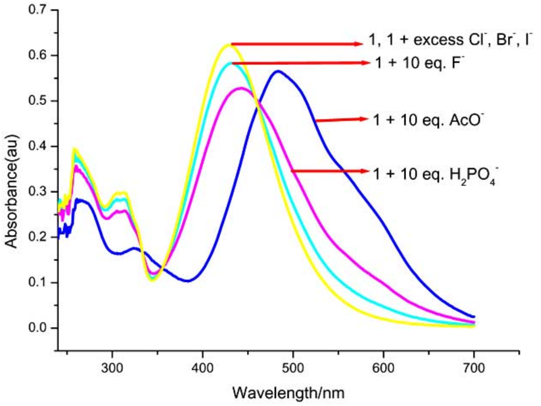


Fig. (1). UV- vis spectra of 1 (1×10^{-5} M) in DMSO in the presence of 10 eq. of AcO^-, F^-, $H_2PO_4^-$, Cl^-, Br^- and I^-.

The investigation of the intrinsic abilities of the sensor **1** were further performed in DMSO solution (1.0×10^{-5} M) containing a serious anions of AcO^-, $H_2PO_4^-$, F^-, Cl^-, Br^- and I^-. Just as shown the Fig. (**3**), in the absence of the anions, there is a maximum absorption centered at 428 nm, with the increasing concentration of AcO^- anion, a new band centered at 483 nm increased obviously and the color of solution changed from little yellow to red. And the UV-vis spectr with addition of F^- and $H_2PO_4^-$ anions are similar with the Fig. (**3**), but the color of solution is changed from little yellow to just little red. The changes of the spectrum demonstrate the formation of acceptor host-anion guest system between the host and anionic guest through hydrogen bond interactions, which affect the electronic properties of the chromophore ($-NO_2$), leading to a new charge transfer between the electron rich –NH group bonded with anion and the electron deficient $-NO_2$ company with color changes [25]. Obviously, there are well-defined isosbestic points centered at 355 nm and 460 nm, which indicate that the stable complexes having a certain stoichiometric ratio between the sensor **1** and AcO^- is indeed formed [26]. And the Job's plot has testified the formation of a 1:1 between 1 and AcO^- (See Fig. **4**). According to the 1:1 stoichiometry, the binding constant (K_{ass}) was calculated to be 1.27×10^5 M, which was shown in the Table **1**, based on the UV-vis absorption spectra. Meanwhile, upon addition of the F^- and $H_2PO_4^-$ anions, which induce the similar spectral changes as with adding AcO^-, however, there are no changes even on adding abundance equiv. of Cl^-, Br^- and I^- anions. Just as shown from Table 1, the order of selectivity or the binding affinity of anions for 1 is $AcO^- > H_2PO_4^- > F^- >> Cl^- \sim Br^- \sim I^-$. However, so far the full understandings of the anion recognition affinities have not been achieved yet.

It is reasonable that in highly affinity anion binding moieties, multiple hydrogen bonding interactions between the sensor and anions should be necessary. In addition, it is also extremely important that the charge and the shape [27] between the host and the anionic guests are complemented. As their basicity, anions AcO^-,

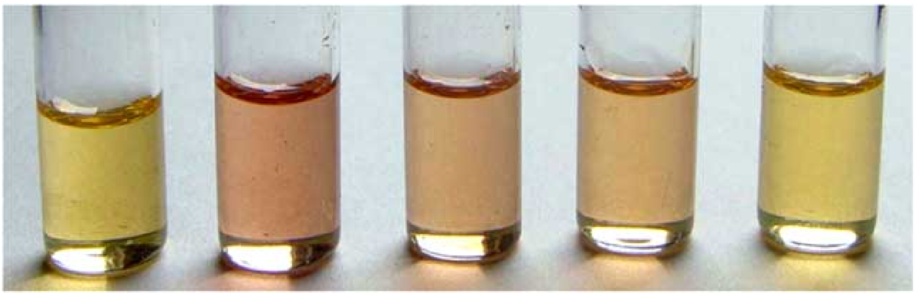


Fig. (2). Color changes of sensor 1 in DMSO (1×10^{-5} M) after addition of 10 eq. anions. A: 1 only; B: 1 + AcO^-; C:1 + F^-; D:1 + $H_2PO_4^-$; E:1 + I^-(similarly, 1 + Cl^-; 1 + Br^-).

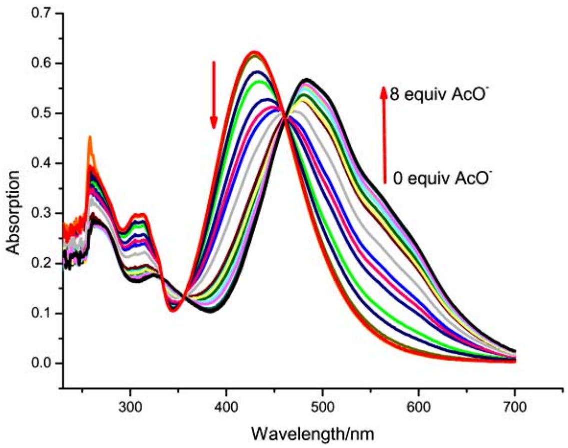


Fig. (3). Changes in the absorption spectrum of 1 (1 × 10^{-5} M) on addition of AcO^- in DMSO.

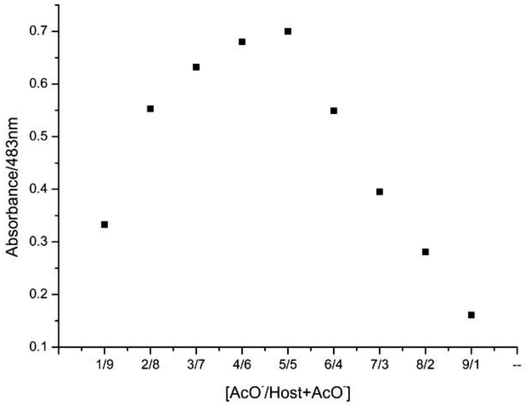


Fig. (4). The stoichiometry analysis of complex 1-AcO^- by the job plot analysis: [1] + [AcO^-] = 10 × 10^{-5} M at 298 K ± 0.1 K.

$H_2PO_4^-$ and F^- generate stronger complexation than other tested anions. Besides, the acetate anion with an O–C–O angle of ca. 120° is a triangular anion and might be the fittest for the two hydrogen atoms on the binding sites of receptor 1, so as to be able to form multiple hydrogen-bonding interactions (See Scheme **2**). This maybe the main reason that the anions of AcO^- can be recognized selectively from the other anions. Accordingly, despite the structures of the other sensors [10, 28] are different with the receptor 1, our works [10, 28 and this] have testified that so long as the receptors contain the sensing sites (=N-NH-), it is able to highly selectively and sensitively recognize the AcO^- in DMSO solution or DMSO/H_2O (95/5) mixture solutions. But the association constant towards fluoride anion is different among these three sensors. The reasons are that, on one hand the sensor **2** [28] interacts with F^- through hydrogen bond forming more stable five member rings than forming six member ring, and on other hand the electron-withdrawing group substituting on phenyl ring (-Br) that simultaneously brings the acidity of the –OH proton stronger to stabilize the hydrogen bonding with the fluoride ion. The sensor **3** and 1 all interact with F^- through hydrogen bond forming six member ring, respectively, but the proton of the indole of sensor **3** [10] takes part in the anions sensing, resulting in the acidity of the proton of the indole is stronger than the acidity of proton of –C*H*=N-NH-. While, the sensor **1** has no strong electron-withdrawing group substitution and the proton of the indole (-NH) does not participate in forming the supermolecule as well. Therefore, the association constant towards fluoride anion for sensor **1** is smallest among three sensors.

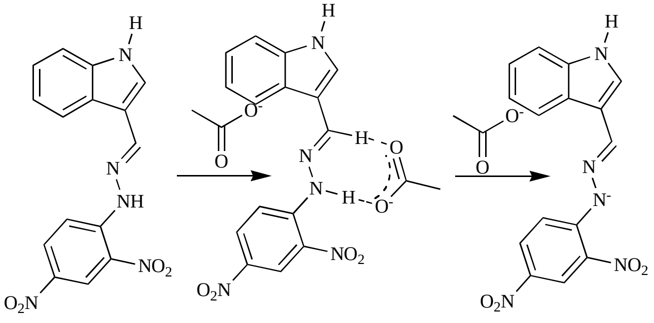
Interestingly, during the titration experiments, the UV-vis spectra still change in DMSO/H_2O (95/5) solutions (1.0 × 10^{-5} M). Upon addition of the AcO^-, $H_2PO_4^-$ and F^- into the mixture solution, the strength of absorbance band centered at 483 nm is gradually increased along with the color changes from little yellow to red (See Fig. **5a**), which is similar as that in dry DMSO solution (See Fig. **5b**). However, the absorption spectrum will not change even the excess amount of the other tested anions are added. Moreover, the anion binding ability was further investigated through UV-vis titrations in aqueous solution and the results exhibited that the addition of small amount of protic solvent like water has almost no effect on the anion sensing properties of compound 1. Consequently, addition of water into DMSO up to 5% could not interfere in the anion recognizing. In fact, the binding affinity of the anions for 1 is possible due to that the compound 1 contains the –NH (Ar-NH-N=) moieties which has been proven to be a good hydrogen bonding acceptor [29] and that the strongly bonding with the anions by hydrogen-bond could not be broken by the addition of 5%(v) water.

Accordingly, the fluorescence titrations were carried out in DMSO solution (1.0 × 10^{-5} M) with the excitation wave lengths at

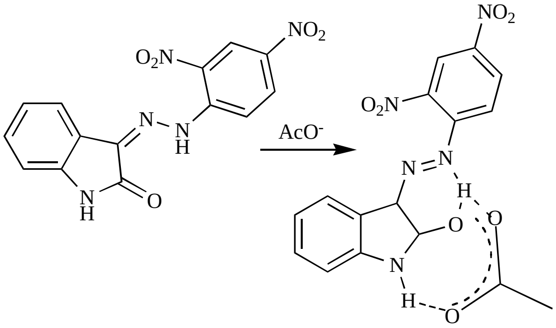
Table 1. Association Constants (K_{ass}, M^{-1}) of the Sensor 1 with Anions in DMSO and DMSO/H_2O (95 /5, v /v) at 298.2 ± 0.1 K

Anions[a]	F^-	AcO^-	$H_2PO_4^-$	Cl^-	Br^-	I^-
$K_{ass}{}^b$	3.75±0.12×10^2	1.25±0.31×10^5	4.42±0.18×10^3	ND[d]	ND	ND
$K_{ass}{}^c$	20.7±0.12	6.01±0.75×10^3	2.30±0.056×10^2	ND	ND	ND

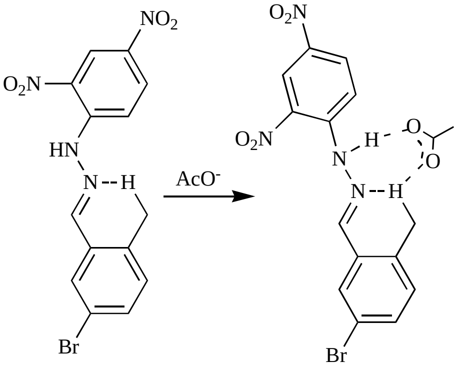
[a] All the anions were added in the form of tetra-n-butylammonium (TBA) salts.
[b] The association constant was determined in DMSO.
[c] The association constant was determined in 95:5 DMSO/H_2O
[d] ND indicates the spectra have too small change after adding anion so we cannot determine the affinity constant by the spectra.



Scheme 2. The proposed host sensor 1-guest binding mode in solution.



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



Sensor 3. The proposed host-guest binding mode in solution.

483 nm. Just as Fig. (**6**), there is a weak emission centered at 520 nm which was gradually quenched with the concentration of AcO$^-$ increased step by step. The possible reason for anions induced the fluorescence quenched is ascribed to the photoinduced electronic transfer (PET) [29] from the indole unit (a fluorophore) to the electron-withdrawing substituent (-NO$_2$), so the fluorescent emission will be little by little quenched upon addition of acetate anions.

To further study the nature of host-guest interactions, ^{1}H NMR spectral changes upon addition of AcO$^-$ in the form of their tetrabutylammonium salts into the DMSO-d_6 solution of 1 (1 × 10^{-2} M) were investigated. Obviously, the proton signals at 11.63 ppm and 11.84 ppm, which were assigned to the –NH moiety of the Indole-3-aldehyde and the (=N-NH-) of the *p*-nitrophenylhydrazone, respectively, were observed in the absence of the AcO$^-$ ions (See Fig. **7**). Upon addition of 0.5 equiv. of AcO$^-$ ions, the signals of the =N-NH- moiety were broadened and the signals on pyrole rings changed slightly. With further addition of AcO$^-$ ions, the phenyl protons especially shifted upfieds significantly, due to the increase of the electron density on the phenyl rings by the through-bond effect. Up to 2 equiv., the –NH proton of the indole shifted downfields and the peaks broadened, which was ascribed to the deprotonation of the amide proton of Ar-CH=N=N*H*-. Consequently, the results of the UV-vis titrations and ^{1}H NMR titrations have testified that the process of anion recognition consists two steps, 1) the receptor 1 interacts with AcO$^-$ ions, 2) the anion induces the deportonation of –NH protons. Accordingly, the UV-vis titrations by adding OH$^-$ anions have also testified the deprotonation of the process (Fig. **8**).

4. ANALYTICAL APPLICATION

In the anion sensing and recognition fields, development of the receptors that can highly selectively and sensitively detect the biologically important anions such as acetate anion in organic solvent even in solutions mixed with protic solvent by effective method

Fig. (5a). Color changes of sensor 1 in DMSO/H$_2$O (95/5) (1×10^{-5} M) after addition of 10 eq. anions. A: 1 only; B: 1 + AcO$^-$; C:1 + F$^-$; D:1 + $H_2PO_4^-$; E:1 + I$^-$ (similarly, 1 + Cl$^-$; 1 + Br$^-$).

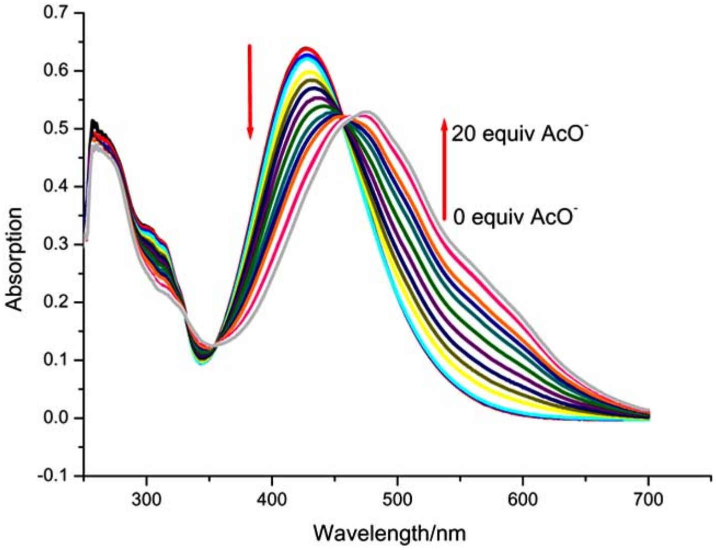


Fig. (5b). Titration of 1 × 10^{-5} M solution of 1 with a standard solution of tetrabutylammonium acetate in 95/5 DMSO / H$_2$O (v:v).

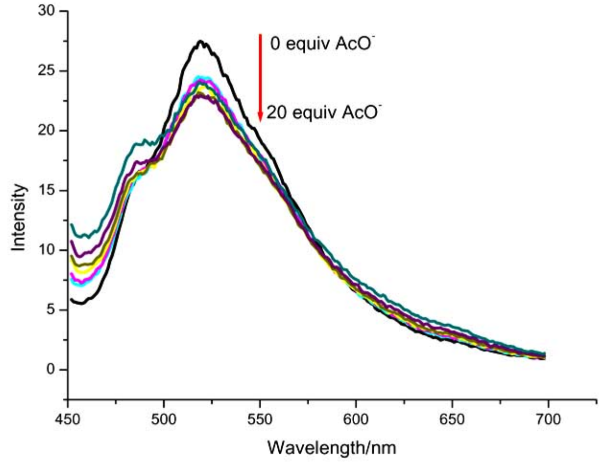


Fig. (6). Fluorescent changes of the sensor 1 in DMSO (1 × 10^{-5} M) upon addition of AcO$^-$ ions.

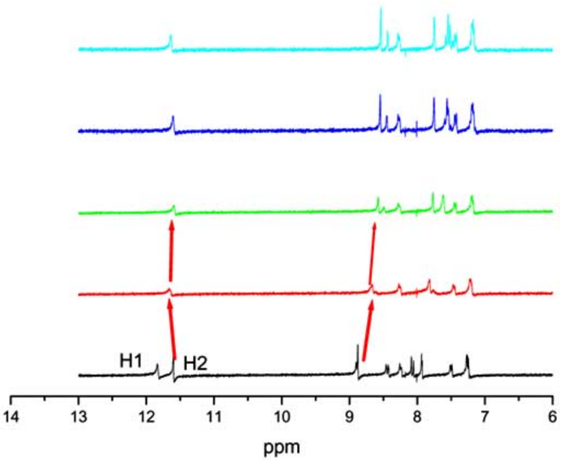


Fig. (7). ^{1}H NMR spectra of the receptor 1 in DMSO-d_6 (1×10^{-2} M) upon addition of molar equiv. of AcO$^-$.

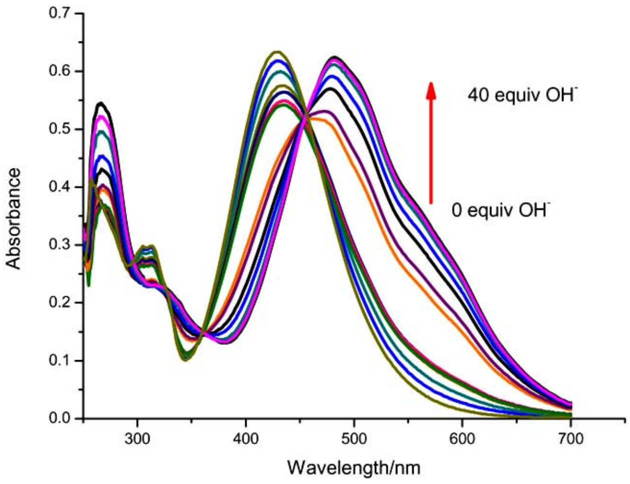


Fig. (8). Titration of 1 × 10^{-5} M solution of 1 with a standard solution of tetrabutylammonium acetate in DMSO solution.

will have greatly important analytical application. The reason is that the acetate anions play an extremely important role in biological, environmental, or organic processes, and so on. Now, the receptor based on the indolealdehyde and 2, 4-dinitrophenylhydrazine was designed, synthesized and studied in DMSO and DMSO/H_2O (95/5) solution. As a result, the color of the solution of the receptor 1 (1 × 10^{-5} M) is changed from yellow to red in the presence of 10 equiv. AcO$^-$, on the contrary, the color will not change noticeably upon addition of F$^-$ and $H_2PO_4^-$ anions, which can be taken advantage of in performing the so-called 'naked-eye' detection to make a distinction between AcO$^-$ and other anions (See Fig. **2**). Significantly, the color of the solution still changes even sensing in the protic solvent DMSO/H_2O (95/5), which provides a potential way to detect anions in the real life. Actually, the receptor 1 exhibits high selectivity to acetate anions as determined by UV-vis titrations using non-linear least square fitting, and the results are displayed in Table **1**. The data show that the affinity constant of the acetate anion is maximal, up to 10^5 M^{-1}. On the other hand, association constant between the AcO$^-$ and receptor 1 is also maximal in the protic solvent DMSO/H_2O (95/5) among other tested anions. All the results indicated that the sensor **1** indolealdehyde hydrazone (compound 1) containing the Indole-3-aldehyde and *2.4*-dinitrophenylhydrazine could be thought as a selective and effective AcO$^-$ anion sensor in the protic solvent DMSO/H_2O (95/5) and would have a potential application in the biological and analytical realm.

CONCLUSION

In summary, we have designed and synthesized a novel anion receptor 1 based on indole and phenylhydrazine, which shows high selectivity to acetate anions in DMSO solvent or DMSO/H_2O (95/5) mixtures. Examination of the binding patterns of the chemosensor by UV-vis and fluorescent titration with a series of anions exhibited obvious changes. The solution color of the sensor is changed from yellow to purple with addition of AcO$^-$, F$^-$ and $H_2PO_4^-$, which could distinguished from other tested anions. Moreover, ^{1}H NMR titrations have indicated that the receptor interacts with anion in the pattern of hydrogen bonding.

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