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A novel acetate selective chromogenic chemosensor based on phenanthroline

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ABSTRACT

A novel colorimetric anion-chemosensor based on 1,10-phenanthroline-2,9-dicarbonyl-*p*-nitrophenylhydrazine has been synthesized. Among the different anions tested, it shows the best selectivity towards AcO^-. The addition of acetate causes the color to change from yellow to red, which could be detected with naked eyes. The binding ability of chemosensor **1** with anions has been investigated through UV–vis spectral titrations. In addition, ^1H NMR experiment was carried out to explore the nature of interaction between chemosensor **1** and acetate.

1. Introduction

It is commonly believed that anions play essential roles in a wide range of chemical, medical and biological processes. For example, carboxylate anion [1–3] exhibits many biochemical functions in the enzymes and antibodies and plays important roles in numerous metabolic processes. Acetate, the unique trigonal carboxylate anion, can form the strong hydrogen-bond when interacting with hydrogen-bond donors. Fluoride primarily plays a significant role in the prevention of dental caries [4]; however, over exposure to fluoride can result in nephrotoxic change in both humans and animals, and lead to urolithiasis [5]. Dihydrogen phosphate anion [6–9] plays a key role in energy storage and signal transduction. Thus, the recognition to anions is of vital importance in the filed of supramolecular chemistry [10,11], and it is necessary to develop selective chemosensors to optically detect anions without resorting to any expensive spectroscopic instrumentation.

In recent years, a number of neutral chromogenic and fluorescent anion chemosensors have been reported. A common approach to obtain such anion chemosensors is to link chromophoric group to the functional group such as amine [1,12–14], urea/thiourea [15], –OH [16] as well as pyrrole [17]. Nitro-substitute phenylhydrazine has been reported as a chromophoric group and hydrogen bonding donor to anions. Our research group has synthesized several colorimetric anion chemosensors by coupling 4-nitrophenylhydrazine with a different chromophore [18–20]. Duan and co-workers have reported a highly selective chromo- and fluorogenic fluoride chemosensor utilizing 2,4-dinitrophenylhydrazine as binding site, which could show naked-eye detection to F^- ion in natural water [21]. Lin has reported a turn-on fluoresecent anion chemosensor based on 1,10-phenanthroline-2,9-diamide (chemosensor **2**, see Scheme 1), which could show high selectivity to F^- ion [22]. Besides that, they have also reported a new chemosensor **3** (see Scheme 1) based on phenanthroline-bridged diamide, which could present high recognition affinity to anions, in particular the fluoride ion [23].

In this paper, we demonstrate a new sensitive AcO^- anion chemosensor in DMSO utilizing hydrazine NH group as binding site, the recognition to anions can be obviously seen from the solution's color change with naked-eye.

2. Experimental

2.1. Apparatus

^1H 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. Chemicals

All reagents for synthesis were obtained commercially and 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

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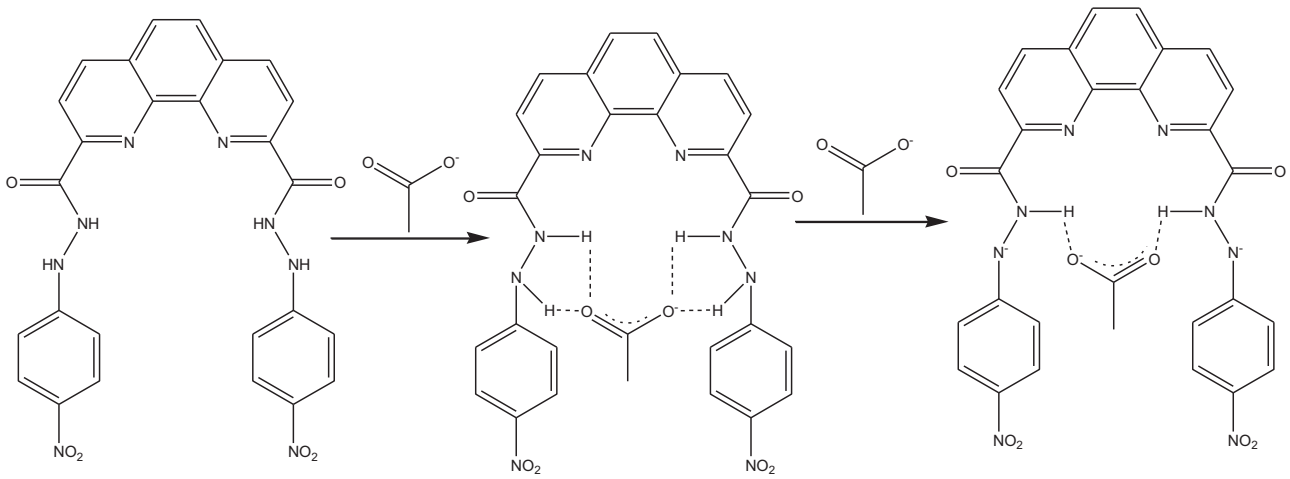

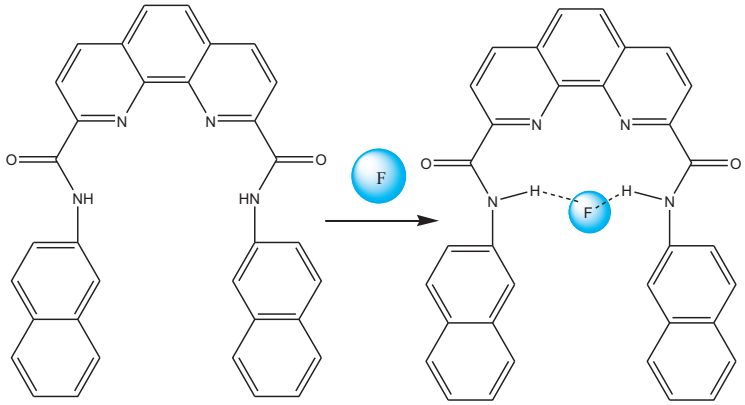

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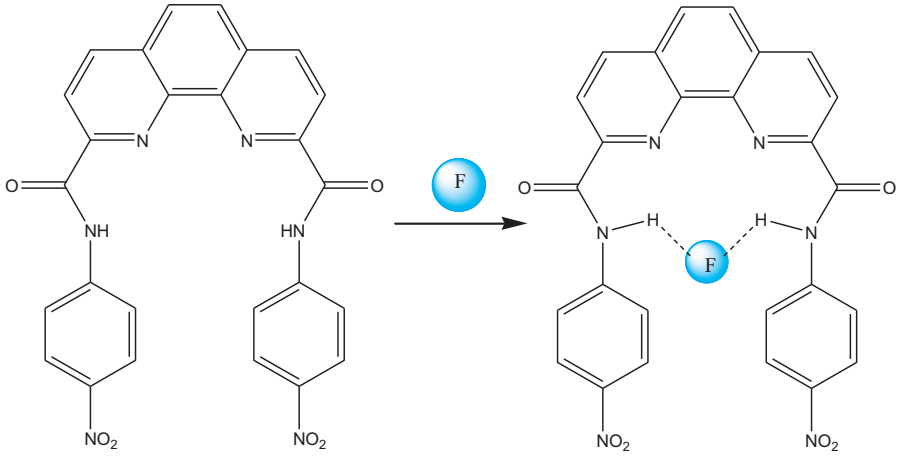
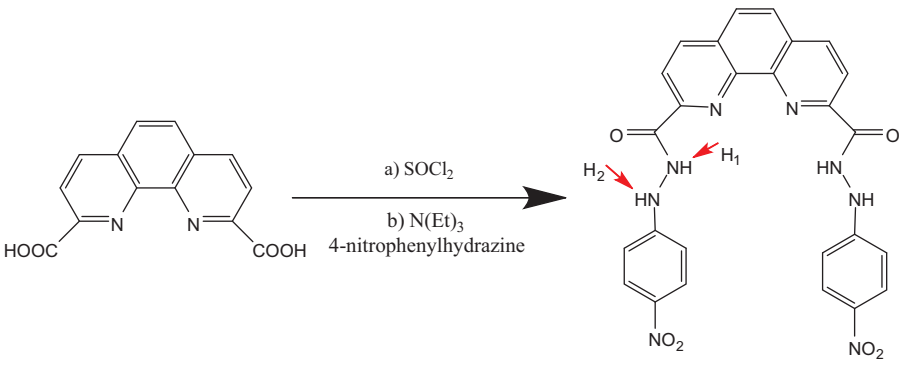


chemosensor 3

Scheme 1. The possible binding model of chemosensor **1** with AcO^-.



Scheme 2. The synthesis of chemosensor **1**.

vacuum desiccator containing self-indicating silica and dried fully before use. DMSO was dried with CaH_2 and then distilled in reduced pressure.

2.3. General method

A 2.0×10^{-3} mol/L solution of chemosensor **1** in DMSO was prepared and stored in the dry atmosphere. Solutions of 1.0×10^{-1} and 1.0×10^{-2} mol/L tetrabutylammonium salt of the respective anion 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 solution (TMS as an internal standard). Certain amount of chemosensor **1** solution in the DMSO-d_6 was prepared with a concentration of 0.01 mol/L. ^{1}H NMR of the host–guest system was recorded by adding increasing amount of acetate anion (1.0 mol/L in DMSO-d_6) into chemosensor **1** solution.

2.4. Synthesis of 1,10-phenanthroline-2,9-dicarbonyl-p-nitrophenylhydrazine (*1*)

The synthesis route of chemosensor **1** is demonstrated in Scheme 2. To 1,10-phenanthroline-2,9-dicarboxylic acid 0.268 g (1 mmol) was added freshly distilled thionyl chloride (25 mL) and the mixture solution was refluxed for 6 h. Then, the solution was concentrated under reduced pressure. The slight yellow residue was dissolved in 25 mL dry CH_2Cl_2 followed by the addition of a catalytic amount of triethylamine. 4-Nitrophenylhydrazine (0.306 g, 2 mmol) was added slowly to the above-mentioned cold mixture solution, stirred for 3 days at room temperature, poured into water, filtered and washed to give 0.33 g pure yellow solid after recrystallization from DMF/CH_3CN (v/v = 7:3). Yield = 60%. ^{1}H NMR (DMSO-d_6): δ11.37 (s, 2H, NH), 9.47 (s, 2H, NH), 8.82 (d, 2H, phen-H), 8.50 (d, 2H, phen-H), 8.30 (s, 2H, phen-H), 8.10 (d, 4H, phenyl-H), 6.93 (d, 4H, phenyl-H); Elemental analysis calcd for $C_{26}H_{18}N_8O_6 \cdot H_2O$: C, 56.04; H, 3.77; N, 16.92. Found C, 56.82; H, 3.77; N, 16.82.

3. Results and discussion

3.1. UV–vis spectral titrations

Firstly, in order to study binding selectivity of the chemosensor **1**, UV–vis titrations have been carried out in DMSO at a concentration of 2.0×10^{-5} mol/L by adding tetrabutylammonium salts of anions. Fig. 1 displays the notable changes in the UV–vis spectrum of chemosensor **1** (2×10^{-5} mol/L) on the addition of AcO^-, $H_2PO_4^-$, Cl^-, Br^- and I^- ions. Obvious spectra changes were observed after adding AcO^- to the solution (see Fig. 1). Moreover, the color of chemosensor **1** solution was changed from yellow to red. However, no detectable spectral responses and color responses were observed even after adding large amount of F^-, $H_2PO_4^-$, Cl^-, Br^- and I^- ions. These results suggest that chemosensor **1** can distinguish acetate from many other anions.

Secondly, to explore more about the applicability of chemosensor **1** for acetate, the UV–vis titrations were performed in DMSO (see Fig. 2). The presence of acetate resulted in the intensity of the absorbance band at 370 nm significantly decreases while the absorbance band at 525 nm increases. The significant spectral changes indicate the internal-molecular charge-transfer (ICT) between anion bonding of the NH structures and the electron-deficient NO_2 moiety [24]. Additionally, as the intensity of the polarization is increased by the $-NO_2$ substituent, the electron density of the hydrazone is transferred to the nitro moiety resulting in the possibility of realizing visual inspection. These results sug-

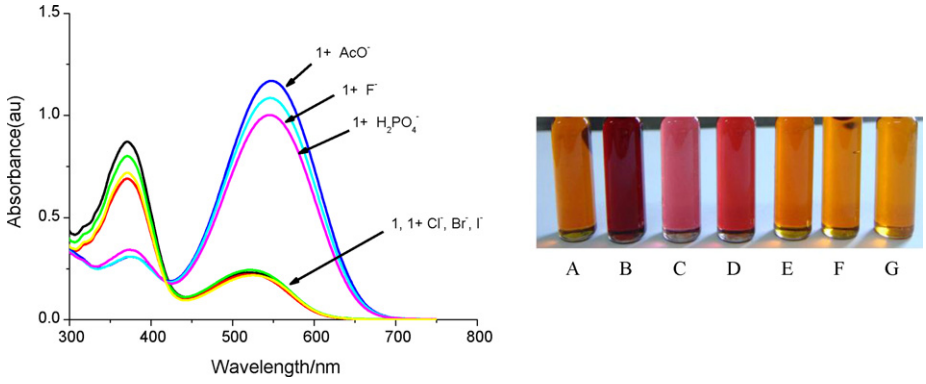


Fig. 1. The left: Absorption spectra of chemosensor **1** (2×10^{-5} mol/L) on the addition of 2.5 equiv. of various anions such as AcO^-, $H_2PO_4^-$, F^-, Cl^-, Br^-, and I^- in DMSO. The right: Color changes of chemosensor **1** in DMSO. [1] = 1.0×10^{-5} mol/L, [anion] = 2.5 equiv.: A = free chemosensor, B = AcO^-, C = $H_2PO_4^-$, D = F^-, E = Cl^-, F = Br^- and G = I^-.

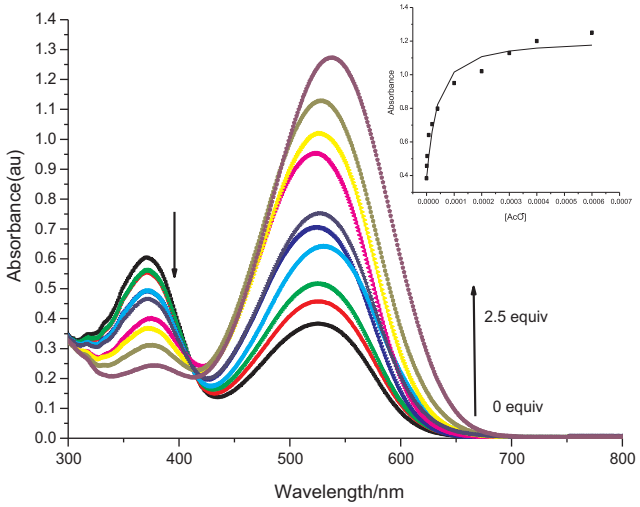


Fig. 2. Evolution of the UV–vis spectra of chemosensor **1** (2.0×10^{-5} mol/L) during the titration with AcO^- in DMSO. Inset: titration plots (observed binding profiles and corresponding non-linear fit plots monitored by the absorption increase at 525 nm).

gest that chemosensor **1** can distinguish acetate from many other anions.

3.2. Determination of affinity constants

To determine the stoichiometry of the host–guest complex, Job's plots have been obtained according to the method reported by Connors [25]. Job's plots of chemosensor **1** and AcO^- in DMSO (see Fig. 3) show the maxima are all at a molar fraction of 0.5. This result indicates that chemosensor **1** binds acetate anion guest with a 1:1 ratio. Moreover, similar results can also be obtained for other anions.

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 [26]. A is the intensity of absorbance at certain concentration of the host and the guest. A_0 is the intensity of absorbance of host only and A_{lim} is the maximum intensity of absorbance of host when gust is added. K is the affinity constant. The affinity constants of chemosensor **1** for the studied anionic species are calculated and

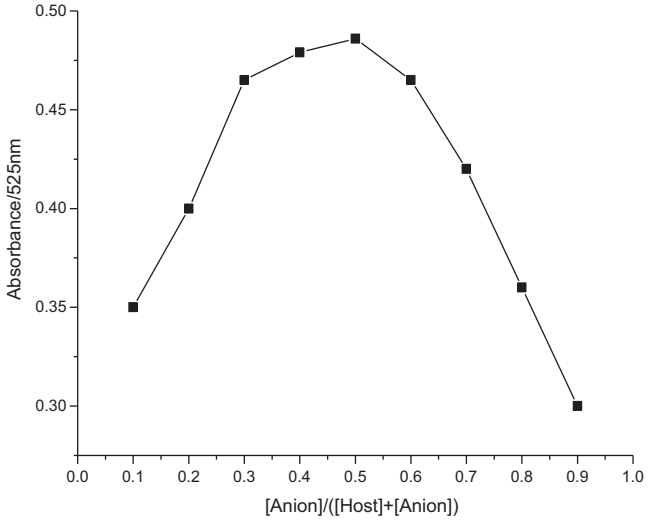


Fig. 3. Job's plot for **1** with AcO^- determined by UV–vis in DMSO, [1] + [anion] = 2.0×10^{-3} mol/L.

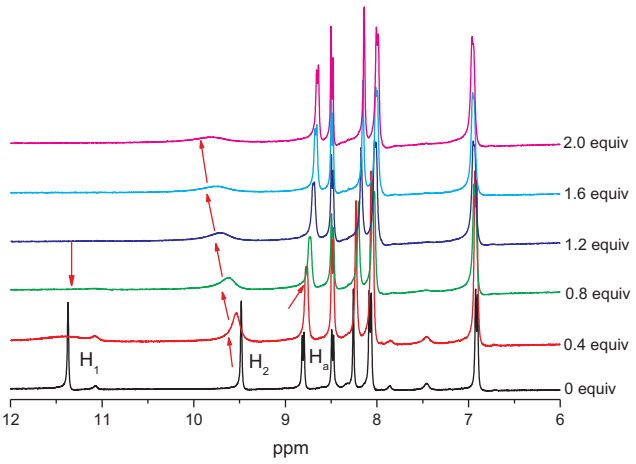


Fig. 4. ^{1}H NMR titration of chemosensor **1** in DMSO-d_6 with AcO^-.

listed in Table 1.

$$X = X_0 + (X_{lim} - X_0)$$

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

Table 1 demonstrates the apparent affinity constants of chemosensor **1** with different anions. As is obviously illustrated in Table 1, the selectivity trends of binding affinities of anions for **1** are determined to be $AcO^- > F^- > H_2PO_4^- \gg Cl^- \sim Br^- \sim I^-$. The main reason for preferring AcO^- is that the triangular shape of AcO^- postures the angle of O–C–O about 120° while the angle of O–P–O of $H_2PO_4^-$ is about 108°, the distance between two oxygen atoms of AcO^- might be more fit for the distance between two –NH of **1**, that is to say the configuration of AcO^- and **1** is better matched [27]. Furthermore, the basicity of AcO^- is stronger, which can form the strongest multiple-hydrogen bonding when interacting with NH groups, thiourea, and amidourea units in acceptor. The affinity constants of Cl^-, Br^-, and I^- are very small due partly to their weak basicity.

Compared with previous literature [22,23], chemosensor **2** [22] without the chromophore like $-NO_2$ group has been only investigated by the fluorescent spectroscopic titrations, not by the UV–vis spectral titrations and the 'naked-eye' detection could not be accessible. In another literature [23], the chemosensor **3** has two binding sites, which shows selectivity for recognizing fluoride. In this paper, we synthesized the new chemosensor **1** containing the chromophore and four binding sites, these advantages contribute to the acetate detection from other anions by 'naked-eye' experiments.

3.3. ^{1}H NMR titrations

To further investigate the interaction mechanism between chemosensor **1** with AcO^- ion, the ^{1}H NMR titration is conducted in the DMSO-d_6 solution of **1** (5×10^{-3} mol/L) to monitor the changes. Two factors that affect the shift of hydrogen are considered. They are the results from the formation of hydrogen bond between the binding moieties of NH sites and the anion. The first factor is that the increased electron density of the phenyl rings can result in proton upfields in the ^{1}H NMR spectrum, and the second factor is that space effects which polarize C–H bond in proximity to hydrogen bond and produce the partial positive charge in the proton can lead to the deshielding effect and downfield shift [28]. Fig. 4 shows the ^{1}H NMR titration spectra of chemosensor **1** with acetate anion. The peaks at 11.371 ppm and 9.472 ppm, which could be attributed to the NH moieties' protons, exhibited an obvious downfield shift upon addi-

Table 1
Association constants of chemosensor **1** with anions in DMSO at 298.2 ± 0.1 K.

Anions[a]	AcO^-	F^-	$H_2PO_4^-$	Cl^-	Br^-	I^-
$K_{ass,1}$	3.84×10^4	1.66×10^4	1.03×10^4	ND[b]	ND	ND
$K_{ass,2}$	2.72×10^2	7.38×10^3	<10	ND	2.66×10^3	ND
$K_{ass,3}$	1.96×10^5	5.64×10^6	ND	3.33×10^5	1.89×10^5	1.24×10^4

[a] All the anions were added in the form of tetra-*n*-butylammonium (TBA) salts.
[b] ND the spectra have too small change with adding anion so we cannot determine the affinity constants by the spectra.

tion of acetate ions. The peak at 11.371 ppm broadened with the addition of 0.5 equiv. acetate anions and completely disappeared with the acetate ions being added up to 1.0 equiv., indicating the fully deprotonation of the $N–H_1$ groups of the host molecule [29]. What is more, the peak at 9.472 ppm just broadens but still exists with further added acetate anion to 2.0 equiv. In addition, the resonance signal of H_1 continues to broaden and shift downfield with further increase in concentration of AcO^- ions, which displays the formation of the hydrogen-bonded chemosensor–anion complexes occurred in the solution. In particular, the aromatic proton especially for the H_a obviously shifts upfield suggesting the increase of the electron density on the phenyl ring due to the through-bond effects. Also, the evidence indicates a higher negative charge and H-bond acceptor tendencies. Such relationship points to the electrostatic nature of chemosensor–oxoanion interaction and rules out any geometrical effect of the binding [29]. Therefore, we propose the anion recognition process as shown in Scheme 1.

4. Conclusions

To sum up, we have presented a simple and colorimetric charge-neutral chemosensor **1**, based on phenanthroline, which could recognize acetate among the anions investigated. The whole processes can be observed with the 'naked-eye', for the color changes from yellow to red, so it is expected to find application detection of acetate in the field of analytical chemistry.

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