

A novel colorimetric sensor for anions recognition based on disubstituted phenylhydrazone

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Abstract Hydrazone-based receptor containing electron-withdrawing chromogenic substituents 1,10-phenanthroline-2,9-di-carboxaldehydic-(2,4-dinitrophenyl)-hydrazone (**1**) has been synthesized. The interaction with different anions via hydrogen bonding was demonstrated by UV-Vis absorption spectroscopy to give a purple 1:1 complexes in DMSO, whose association constant decreases in line with the following order of the studied anions ($\text{AcO}^- > \text{F}^- > \text{H}_2\text{PO}_4^- > \text{OH}^- \gg \text{Cl}^- \sim \text{Br}^- \sim \text{I}^-$). As a naked-eyes colorimetric sensor for anions, the study has a latent application importance.

Keywords Colorimetric chemosensor · Hydrazone · Phenanthroline · Anion recognition

Introduction

The design of new receptors with electrochemical or optical properties for the selective detection of anions has received considerable attention over the past several years, for anions not only are ubiquitous throughout biological systems but also play crucial roles in the areas of medicinal, catalysis, and environmental chemistry. Nowadays, the development of colorimetric anion sensing is particularly challenging since it requires the use of inexpensive equipment or no equipment at all as color changes can be

detected by the naked eye [1]. Visual detection can give immediate qualitative information and is becoming increasingly appreciated in terms of quantitative analysis [2–9]. In fact, there are many examples of analytical determinations whose final step involves the formation of a colored compound which indicates the initial concentration of a certain analyte. This is so basically for cations and in a minor coverage for anions. The chromogenic sensors for anions generally consist of two parts: anion receptors and chromophores. Typically, a colorimetric sensor is constituted by a chromogenic subunit covalently linked to a receptor. Neutral receptors donate to the anion hydrogen-bond-donor groups, in most cases the $-\text{NH}$ fragment of carbonylamides, sulfonamides, ureas, thioureas and pyrroles [7, 9, 10, 11]. In anion coordination chemistry, the $\text{N}-\text{H}$ fragment of a receptor can be further polarized, and its H-bond donor tendency increased, through introducing the molecular framework of electron-withdrawing substituents (e.g., $-\text{NO}_2$, CF_3) or positively charged groups (e.g., alkylpyridinium). However, this procedure may be risky: In fact, extreme polarization may lead to the occurrence of a definitive proton transfer from the receptor to an especially basic anion, which forms a feature that pushes the anion out of the supramolecular control of the receptor and extrudes the operator from the discipline of supramolecular chemistry. Those studies are well done by Luigi Fabbrizzi et al. in the recent years [11, 12]. Compared with well-known types of hydrogen bonding for the anion with amides, pyrroles, and ureas and sulfonamide, phenylhydrazone-based receptors for anions are rare though they have strong binding ability with anions and are readily available. To the best of our knowledge, a few colorimetric sensors for acetate ion have been reported [13–15] even though a lot of that for fluoride ion has been designed [16–21] according to this principle.

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In this paper, we present a novel colorimetric receptor **1** (Fig. 1) based on two –NH fragments in which contains two hydrazone groups designed as the binding sites and nitro being electron-withdrawing substituent, which shows a high selective binding ability to the acetate ion over other studied ions. The proposal interaction process between the receptor and acetate anion was characterized by ^1H NMR titration. All of the optical properties for the selective detection were carried out in aprotic media (DMSO).

Experimental

Reagents

All anion, in the form of tetrabutylammonium salts, were purchased from Sigma-Aldrich Chemical Co., stored in a desiccator under vacuum containing self-indicating silica, used without any further purification and dried with P_2O_5 in vacuum desiccator at 353 K for 24 h prior to use. Dimethyl sulfoxide was dried with calcium hydride and distilled at reduced pressure prior to use. Unless stated otherwise, A R grade chemicals were purchased and used without further purification. The 1,10-phenanthroline-2,9-dicarboxaldehyde was prepared according to the well-known method [22].

Instruments

Elemental analyses for C, H, and N were carried out on a Perkin Elmer 240 C element analyzer at Institute of Elemento-Oganic Chemistry, Nankai University. The ^1H NMR spectra were recorded using a Varian UNITY-plus 400 MHz spectrometer at the State Key Laboratory of Functional Polymer Materials for Absorption and Separation, Nankai University. UV-Vis absorption spectra were

performed on a UV-2450 spectrophotometer of SHIMA-DZU. The spectrophotometer was standardized.

Synthesis

1,10-phenanthroline-2,9-di-carboxaldehydic-(2,4-dinitrophenyl)-hydrazone (**1**), 1,10-phenanthroline-2,9-dicarboxaldehyde (0.47 g, 2 mmol) and 2 equivalents of 2,4-dinitrophenylhydrazine was added in ethanol (50 mL) and refluxed for 6 h. The mixture was filtered while hot, washed with ethanol to give an orange solid which was recrystallized from DMF to yield 0.79 g (yield 62.2%).

^1H NMR (DMSO- d_6): δ 11.35(s, 2H, NH), 8.78(d, 2H, phen-H, $J = 8.2$ Hz), 8.47(d, 2H, phen-H, $J = 8.0$ Hz), 8.21(d, 2H, phen-H, $J = 8.1$ Hz), 7.46(s, 2H, Ar-H), 7.11(d, 4H, Ar-H, $J = 8.1$ Hz), 5.45(s, 2H, CH). Anal. Calcd. for $\text{C}_{26}\text{H}_{16}\text{N}_{10}\text{O}_8 \cdot 2\text{H}_2\text{O}$: C: 49.37, H: 3.19, N: 22.14. Found: C: 49.14; H: 3.35; N: 21.97.

Results and Discussions

Spectrophotometric titrations were performed on 5.0×10^{-6} mol/dm 3 solutions of receptor **1** in dimethyl sulfoxide (redistilled before use). Typically, increasing concentration (1–100 equiv.) of a fresh tetrabutylammonium salt standard solution of the required anion F^- , Cl^- , Br^- , I^- , AcO^- , H_2PO_4^- or OH^- was added respectively, and the UV-vis absorptions of the samples were recorded.

We observed that, with the addition of an excess of a few equivalents of AcO^- , F^- , H_2PO_4^- or OH^- , the color of a DMSO solution of **1** turned from yellow to purple. No color changes occurred in case of when the receptor **1** was treated with Cl^- , Br^- and I^- (see the color change of the photograph in Fig. 2).

For all of the anions studied, AcO^- , F^- , H_2PO_4^- and OH^- anions are capable of changing the UV/vis intensity. Figure 2 shows the family of spectra recorded on titrating a DMSO solution 5.0×10^{-6} mol/dm 3 of **1** with a standard DMSO solution of sensitive anions (e.g., **1** interacts with acetate). When acetate anion was introduced to the solution of **1**, the intensity of the band at 407 nm decreases while a new absorption peak was observed at 558 nm (F^- at 547 nm; H_2PO_4^- at 552 nm and OH^- at 567 nm) and the UV/vis intensity was gradually increased, the color of the solution turning from yellow to purple as the sensitive anions concentration increased which indicated that a strong binding interaction took place between the anions and the receptor **1** (see spectra in Fig. 3 and color change in Fig. 2). The satisfactory result of non-linear curve fitting confirmed that **1** and sensitive anions formed 1:1 complexes (Non-linear curve of molar absorbance at 558 nm vs. equivalent of acetate anion has been inserted in Fig. 3).

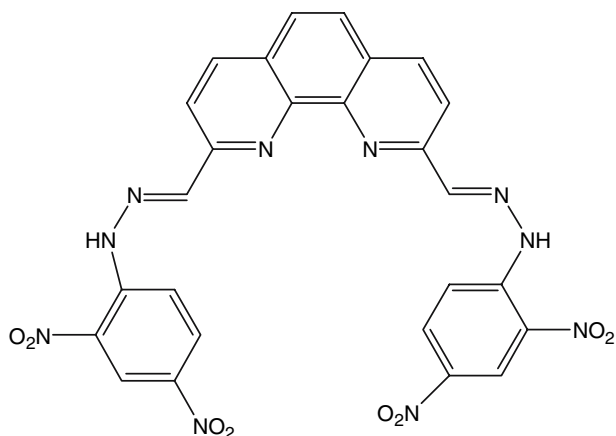
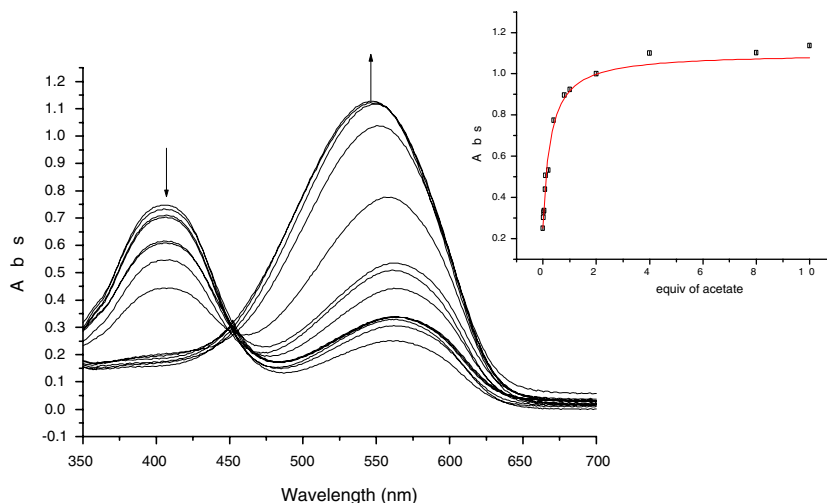


Fig. 1 Structure of receptor **1**

Fig. 2 Color changes observed with addition of different anions to a DMSO solution of receptor **1**. a: free receptor **1**; b: **1** + F⁻; c: **1** + Cl⁻; d: **1** + Br⁻; e: **1** + I⁻; f: **1** + AcO⁻; g: **1** + H₂PO₄⁻; h: **1** + OH⁻; (Plus 100 equiv. of studied anions)



Fig. 3 Family of spectra recorded on titrating a DMSO solution 5.0×10^{-6} mol/dm³ of **1** with a standard DMSO solution of acetate ion at 298 K. The equivalents of acetate are from 0 to 10; (inserts: titration profiles of the band at 558 nm, R² of non-linear curve fitting is 0.9808)



Under the same conditions, there were no significant changes with spectrum and color upon the addition of tetrabutylammonium chloride, bromide, iodide ion even in the presence of high concentration of anions (>1000 equiv.).

Continuous variation method was used to determine the stoichiometric ratio of the receptor **1** and sensitive anions. Figure 4 shows Job plots of the difference between the observed absorbance and the absorbance of the free

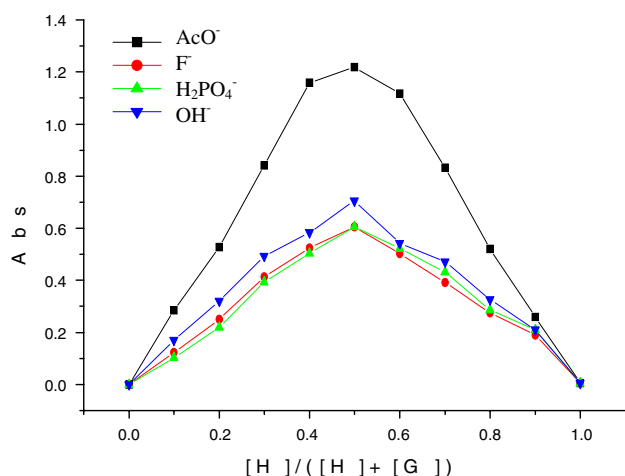


Fig. 4 Job plots of receptor **1** with sensitive anions, total concentration of the host and guest is 1.0×10^{-5} mol/dm³ (AcO⁻ at 558 nm; F⁻ at 547 nm; H₂PO₄⁻ at 552 nm; OH⁻ at 567 nm)

receptor **1**, with the molar fraction of host continuously varying [23]. The results illustrate that **1**-anion complexes concentration approaches a maximum when the molar fraction of host $\{[H]/([H] + [G])\}$ is about 0.50, meaning that the receptor formed 1:1 complex with the sensitive anions.

For a complex of 1:1 stoichiometry, the relation in Eq.(1) could be derived easily, as reported formerly, where X is the absorption intensity, and c_H or c_G is the concentration of host or anion guest correspondingly [24]. The association constant was determined by nonlinear fitting analyses of the titration curves according to the Eq. (1).

$$X = X_0 + (X_{lim} - X_0) \frac{c_H + c_G + 1/K_{acc}}{\left\{ [c_H + c_G + 1/K_{acc}]^2 - 4c_H c_G \right\}^{1/2}} \quad (1)$$

The result of association constant of receptor **1** for studied anions was shown in Table 1. The receptor **1** can recognize acetate anion with high selectivity than other anions studied (about over 10 times), which is better than some fluorogenic receptors or colorimetric sensors reported previously [12–14].

The structural characterization of the interaction process between the receptor and acetate anion was further supported by the ¹H NMR titration (Fig. 5). The ¹H NMR spectral changes was observed upon addition of

Table 1 LogK_{acc} for 1:1 complex of receptor **1** with anions in DMSO at 298 K

Anion	F ⁻	Cl ⁻	Br ⁻	I ⁻	AcO ⁻	H ₂ PO ₄ ⁻	OH ⁻
logK _{acc}	4.95(± 0.01)	—*	—	—	5.86(± 0.01)	4.85(± 0.02)	4.69(± 0.03)

* The reliable K_{acc} couldn't be obtained due to little changes of intensity

tetrabutylammonium salt of AcO⁻ to the solution of receptor **1** (5.0×10^{-3} mol/dm³). A cursory glance of ¹H NMR spectral change reveals that the resonances ascribable to the NH proton of receptor **1** (11.35 ppm) initially broadened upon successive addition of acetate anion and finally appeared at [1]: [AcO⁻] = 1:2. The CH proton shifted downfield from 5.45 ppm to 5.75 ppm. This result indicates that the NH has suffered a deprotonation processes and a potential hydrogen bond has been formed between N = CH proton and acetate anion.

The result shows that binding ability of receptor **1** to anions maybe contribute to its basicity and geometry configuration. 1,10-phenanthroline-2,9-di-carboxaldehydic-(2,4-dinitrophenyl)-hydrazone has a high selectivity for triangular anion (AcO⁻). The two oxygen atoms of acetate (triangular) have bind with two hydrogen atoms of -CH via hydrogen bond since the angle of two oxygen atoms is 120° and the distance of two oxygen atoms maybe fit to the two hydrogen atoms on the cavity plane of receptor **1** in the triangular configuration (Fig. 6). The angle of two oxygen atoms is 108° for H₂PO₄⁻ (tetrahedral configuration), the distance of two oxygen atoms of H₂PO₄⁻ is less than that of AcO⁻, two oxygen atoms of H₂PO₄⁻ can not be fit to two hydrogen atoms in receptor **1** as AcO⁻. The OH⁻ (linear molecule) only has an oxygen atom which can't be fit to two hydrogen atoms of -CH in receptor **1**. This is the most possible cause why the binding ability of AcO⁻ is higher than H₂PO₄⁻ and OH⁻. Also another evidence indicated that the higher the negative charge, the higher the H-bond

acceptor tendency of the anion [19]. On the other hand, the ability of binding for spherical anions such as halides is related to the basicity and size of the anion. Fluoride, smallest anion, has unique chemical properties. The receptor **1** with a cleft forming a rigid cavity by two rigid arms would bind preferably with anions through effective hydrogen bonding. The cleft between the hydrogen of N-H in the receptor **1** is able to bind small anions well, such as fluoride. The selectivity for fluoride of binding ability among halides also contributes to the high basicity and electro negativity of fluoride.

Conclusion

In summary, the anions receptor **1** based on the dihydrazones containing -NH binding sites of selectively sensing anions has been synthesized. It interacts via hydrogen bonding with different anions were demonstrated by UV-Vis absorption spectroscopy to give a purple 1:1 complexes in DMSO, whose stability decreases with the following order of the studied anions (AcO⁻ > F⁻ > H₂PO₄⁻ > OH⁻ >> Cl⁻ ~ Br⁻ ~ I⁻). The binding ability of receptor **1** to anions maybe contributes to its basicity and geometry configuration. The study has a latent application importance to be a naked-eyes colorimetric sensor for anions.

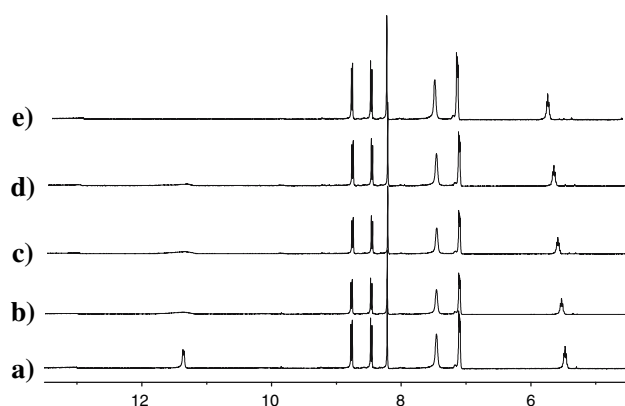


Fig. 5 ¹H NMR spectra obtained in the course of the titration of a solution of **1** in DMSO (5×10^{-3} mol/dm³) with AcO⁻, a) free **1**, b)–e): 0.5, 1.0, 1.5, 2.0 equiv. AcO⁻ of **1**

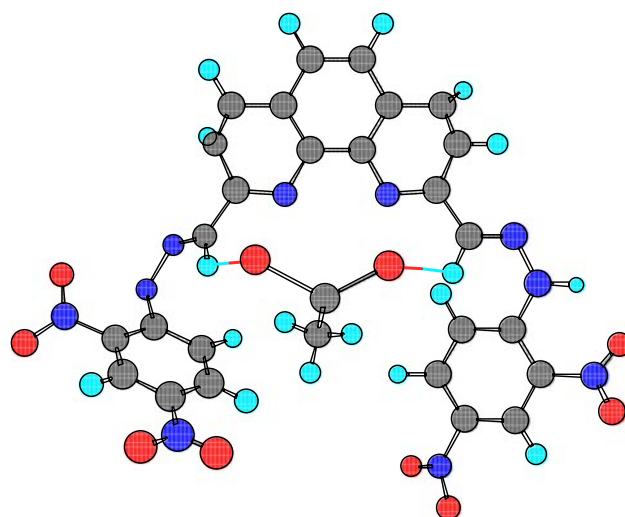


Fig. 6 The proposed molecular model of the receptor-acetate complexes

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