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A highly selective naked-eye colorimetric sensor for acetate ion based on 1,10-phenanthroline-2,9-dicarboxyaldehyde-di-(p-substitutedphenyl-hydrazone)

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ABSTRACT

A new and simple colorimetric sensor with high selectivity for acetate ion based on 1,10-phenanthroline-2,9-dicarboxyaldehyde-di-(p-substitutedphenylhydrazone) receptor **2** has been synthesized. The selectively binding ability of receptor **2** to acetate ion over other anions tested was demonstrated by UV–vis absorption spectroscopy in DMSO. Comparing with other anions studied, the UV–vis absorption spectrum in dimethyl sulfoxide shows significant response toward acetate ion with high selectivity, and meanwhile dramatic color change is observed from yellow to green in the presence of acetate ion (5×10^{-6} mol/L). Little UV–vis absorption spectrum change has occurred when receptor **2** was titrated with other different guest (F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$ and OH^-). In addition, the ^1H NMR spectrum titration shows deprotonation of the receptor in the presence of acetate ion.

1. 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, as anions are ubiquitous throughout biological systems and play crucial roles in the areas of medicinal, catalysis, and environmental chemistry. Nowadays, the development of colorimetric anion sensing is particularly attractive since it does not require expensive equipment as color changes can be easily 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]. 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. In general, binding sites are the hydrogen-bond-donor groups, in most cases the –NH fragment of carboxyamides, sulfonamides, ureas, thioureas and pyrroles [7,9,10]. Compared with well-known hydrogen-bonding sites such as amides, pyrroles, and ureas and sulfonamide, hydrazone-based receptors for anions are rare, but they have strong binding ability with anions and are readily available.

In anion coordination chemistry, the N–H fragment of a receptor can be further polarized, and its H-bond donor tendencies increase, through the insertion onto the molecular framework of electron-withdrawing substituents (e.g., $-NO_2$, CF_3) or positively charged groups (e.g., alkylpyridinium). In addition, the binding ability with anions can be significantly improved at the same time. To the best of our knowledge, a few colorimetric sensors for acetate ion have been reported [11,12] though a lot of that for fluoride ion have been designed [12–17] according to this principle.

In this paper, we present two new colorimetric receptors **1** and **2** (Scheme 1) based on two –NH fragments in which contains two hydrazone groups as the binding sites. Receptor **2** with $-NO_2$ units being electron-withdrawing substituents shows a high selective binding ability to the acetate ion over other studied ions. All of the optical properties for the selective detection were carried out in aprotic media (DMSO).

2. Experimental

2.1. Reagents

All anions, in the form of tetrabutylammonium salts, were purchased from Sigma–Aldrich Chemical Co., stored in a desiccator under vacumm containing self-indicating silica, used without any further purification and dried with P_2O_5 in vacumm 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 [18].

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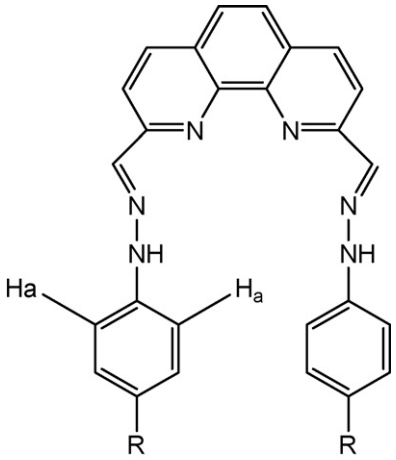

1 R=H

2 R=NO_2

Scheme 1. Structure of sensors.

2.2. Instruments

Elemental analyses for C, H, and N were carried out on a PerkinElmer 240C element analyzer at Institute of Elemento-Oganic Chemistry, Nankai University. The ^{1}H 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 SHIMADZU. The spectrophotometer was standardized.

2.3. Synthesis

2.3.1. 1,10-Phenanthroline-2,9-dicarboxyaldehyde-diphenylhydrazone (*1*)

1,10-Phenanthroline-2,9-dicarboxaldehyde (0.47 g, 2 mmol) and 2 equiv. of phenylhydrazine 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 0.55 g (yield 60.1%). ^{1}H NMR (DMSO-d_6):δ 10.62 (s,2H,NH), 8.78 (d,2H,phen-H), 8.64 (m,2H, phen-H), 8.46 (d,2H,phen-H), 7.84 (s,2H,CH), 7.44 (d,4H, phenyl-H), 7.32(m,6H phenyl-H). Anal. Caled. for $C_{26}H_{20}N_6{\cdot}H_2O$: C, 71.89; H, 5.07; N,19.35. Found: C, 71.45; H, 4.86; N, 14.96.

2.4. 1,10-Phenanthroline-2,9-dicarboxyaldehyde-di-(p-nitrophenylhydrazone) (*2*)

The receptor **2** was prepared by a similar procedure to the above. 1,10-Phenanthroline-2,9-dicarboxaldehyde (0.47 g, 2 mmol) and 2 equiv. of p-nitrophenylhydrazine was added in ethanol (50 ml) and refluxed for 4 h. The mixture was filtered while hot, washed with ethanol to give a red solid which was recrystallized from DMF to yield 0.68 g (yield 68%). ^{1}H NMR (DMSO-d_6): δ 11.92 (s,2H,NH), 8.78 (d,2H,phen-H), 8.64 (m,2H, phen-H), 8.46 (d,2H,phen-H), 8.22 (d,4H, phenyl-H), 7.84 (s,2H,CH), 7.42 (d,4H phenyl-H). Anal. Caled. for $C_{26}H_{18}N_8O_4{\cdot}H_2O$: C, 59.54; H, 3.82; N,21.37. Found: C, 59.79; H, 3.88; N, 21.86.

3. Results and discussion

3.1. UV–vis titration

Spectrophotometric titrations were performed on 5.0×10^{-6} mol/dm^3 solutions of receptor **1** and **2** in dimethyl sulfoxide (redistilled before use). Typically, increasing concentration (1–20 equiv.) of a fresh tetrabutylammonium salt standard solution of the required anion F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$ and OH^- were added, respectively, and the UV–vis absorptions of the samples were recorded.

On addition of 5 equiv. of AcO [NBu_4], the color of a DMSO solution of **2** turned from yellow to green. The color changes were not observed at all when the receptor **2** was treated with other anions (see the photograph in Fig. 1). However, receptor **1** has no color changes resulting from addition of all anions studied.

Fig. 2 shows the family of spectra recorded by titrating a DMSO solution 5.0×10^{-6} mol/dm^3 of **2** with a standard DMSO solution of acetate ion. Among all of the anions tested, only acetate anion can result in the changes in the UV–vis spectrum. When acetate anion was introduced to the solution of **2**, the intensity of the band at 447 nm decreases while a new absorption peak at 613 nm was observed and gradually increased, the color of the solution turning from yellow to green as the acetate ion concentration increased which indicated that there was a strong binding interaction between the acetate ion and the receptor **2** (see spectra in Fig. 2 and color change in Fig. 1). The satisfying result of nonlinear curve fitting (absorbance at 613 nm against equivalent of acetate ion) confirmed that there formed the stable complex having a certain stoichiometric ratio between the receptor **2** and AcO^- anion, which would be further confirmed by the Job plot. Under the same conditions, there were no significant changes in spectrum and color even in the presence of high concentration of anions such as fluoride, chloride, bromide, iodide, dihydrogen phosphate and hydroxide ions. These results suggest that the receptor **2** can provide a high selectivity for the acetate ion among the studied anions.

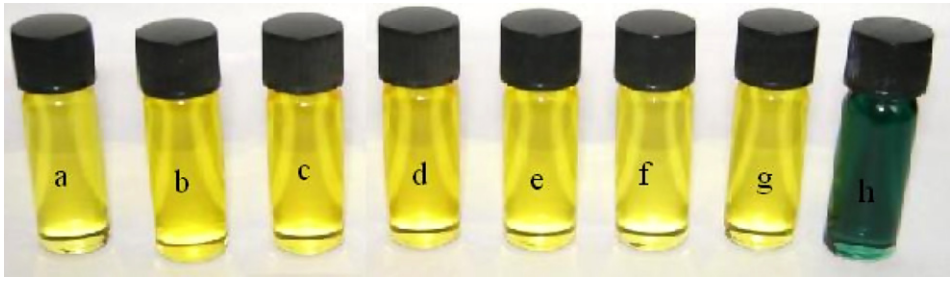

Fig. 1. Color changes observed on addition of different anions to a DMSO solution of receptor **2**: (a) free receptor **2**; (b) **2** + F^-; (c) **2** + Cl^-; (d) **2** + Br^-; (e) **2** + I^-; (f) **2** + $H_2PO_4^-$; (g) **2** + OH^-; (h) **2** + AcO^- (plus 5 equiv. of studied anions).

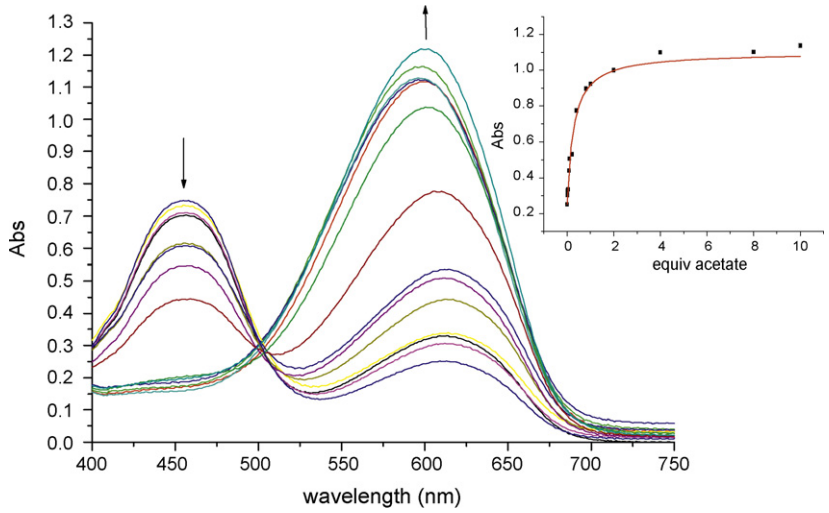

Fig. 2. Family of spectra recorded on titrating a DMSO solution 5.0×10^{-6} mol/dm^3 of **2** with a standard DMSO solution of acetate ion at 25 °C; insert: titration profiles of the bands at 613 nm, which correspond to the hydrogen-bond complex [2 AcO]$^-$.

Similar changes were not observed when the anions were added to the solution of the receptor **1**, which shows that **1** has no binding ability for all studied anions. This indicates that the N–H fragment of a receptor can be further polarized, and its H-bond donor ability was improved, through the insertion onto the molecular framework of electron-withdrawing substituents (e.g., $-NO_2$, CF_3).

Continuous variation method was used to determine the stoichiometric ratio of the receptor **2** and acetate ion. Fig. 3 shows Job plot of the difference between the observed absorbance and the absorbance of the free receptor **1** (613 nm with the molar fraction of host {[H]/([H]+[G])} for a series of solutions in which the total concentration of host and acetate anion was constant (1.0×10^{-5} mol/dm^3), with the molar fraction of host continuously varying [19]. The result illustrates that 2-acetate complex concentration approaches a maximum when the molar fraction of host {[H]/([H]+[G])} is about 0.50, meaning that the stoichiometry of the 2-acetate interaction was confirmed to be 1:1 from the Job plot.

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 [20] The association constant was determined by nonlinear fitting analyses of the titration curves according to Eq. (1). The K_{ass} of receptor **2** binding with acetate ion is 3.06×10^5:

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

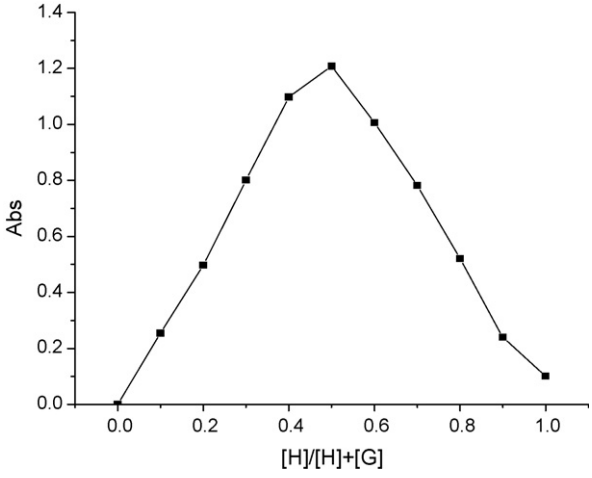

Fig. 3. Job plot of receptor **2** with acetate at 613 nm; the total concentration of the host and guest is 1.0×10^{-5} mol/dm^3.

Non-linear curve of molar absorbance at 613 nm versus equivalent of acetate anion has been inserted in Fig. 2. The result of association constant of receptors **1** and **2** for anions was shown in Table 1. The receptor **2** can recognize acetate anions with high selectivity than other anions studied.

Particularly, the result shows that the receptor **1** has no ability to bind anions and the receptor **2** with $-NO_2$ groups has a high selectivity for triangular anion (AcO^-) among the anions tested such as F^- and $H_2PO_4^-$. In general, Detection or recognition of acetate ion can be interfered by the other strong basic anions such as F^- and $H_2PO_4^-$ [11,12,21]. In other words, the single receptors with high recognition for acetate ion were rarely reported in the literature. For example, Jang et al. [22] successfully showed a colorimetric anion chemosensor based on 2-aminobenzimidazole for acetate. Unluckily, their receptor had no ability of recognizing acetate from F^- only through naked-eye. The receptor 2 exhibited color response only to AcO^- and addition of the other anions such as F^- and $H_2PO_4^-$ resulted in no color changes of solution of the receptor **2** (see Fig. 1). To best of our knowledge, such sensors were not found in the literature. Therefore, the compound **2** could act as a high selective and colorimetric sensor for naked-eye detection of AcO^- in organic medium.

3.2. ^1H NMR titration

The interaction of receptor **2** with acetate (used as tetrabutylammonium salt) was investigated by ^1H NMR spectroscopy in DMSO-d_6. In particular, a 1.0×10^{-3} M DMSO-d_6 solution in 2 was titrated with AcO^-, which was added stepwise up to 2 equiv. Fig. 4 shows the different patterns of ^1H NMR spectra obtained in the course of the titration. In fact, the –NH proton (11.47 ppm) initially broadened and finally disappeared while C–H_a protons of the phenyl rings shifted upfield (from 7.21 ppm to 7.05 ppm) in the 0–2 equiv. ranges. The CH proton shifted downfield from 5.74 ppm to 5.74 ppm. This result indicates that the NH proton 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 **2** maybe contributed to its basicity and geometry configuration. Receptor **2** has a

Table 1
K_{ass} for 1:1 complex of receptor 1 with halide anions in DMSO at 298 K.

Anion[a]	F^-	Cl^-	Br^-	I^-	AcO^-	$H_2PO_4^-$	OH^-
K_{ass} of **1**	–[b]	–	–		<100	–	–
K_{ass} of **2**	–	–	–	–	3.06×10^5	–	–

[a] The anions were added as their tetrabutylammonium salts.
[b] The reliable K_{ass} could not be obtained due to little changes of intensity.

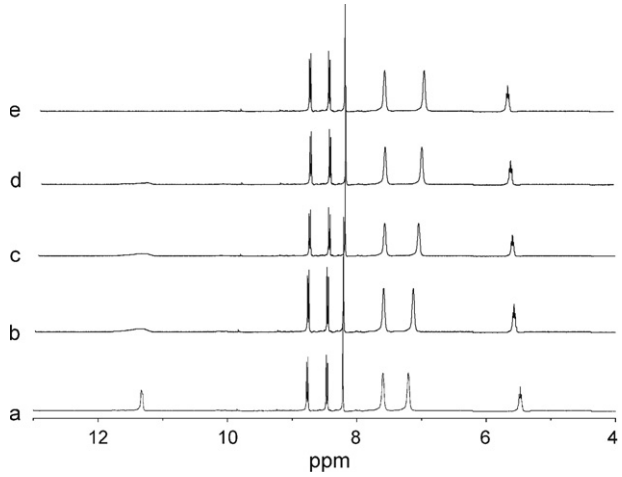

Fig. 4. ^1H NMR spectra taken in the course of the titration of a DMSO-d_6 solution 1.0×10^{-3} m in receptor **2** (a) with a standard solition of acetate: (a) free receptor; (b) **2** + 0.25 equiv. of acetate; (c) **2** + 0.5 equiv. of acetate; (d) **2** + 1 equiv. of acetate; (e) **2** + 2 equiv. of acetate.

high selectivity for triangular anion (AcO^-). The two oxygen atoms of acetate have bind with two hydrogen atoms of –CH via hydrogen bond since angle of two oxygen atoms is 120° and the distance of two oxygen atoms maybe fit to the two oxygen atoms on the cavity plane of receptor **2** in the triangular configuration. The angle of two oxygens is 108° for $H_2PO_4^-$ (tetrahedral configuration), the distance of two oxygens of $H_2PO_4^-$ is less than AcO^-, two oxygens of $H_2PO_4^-$ cannot be fit to two hydrogens which can form hydrogens bond with AcO^- in receptor **2**. The OH– (linear molecule) only has one oxygen which cannot be fit to two hydrogens of –NH in receptor **2**. This is the most possible reason why the binding ability of AcO^- is much higher than $H_2PO_4^-$ and OH^-. Also another evidence indicated that the higher the negative charge, the higher the H-bond acceptor tendencies of the anion. The existence of such a relationship points toward the electrostatic nature of the receptor–oxoanion interaction and rules out any geometrical effect on the binding (e.g., matching of the distance of the N atoms of the receptor subunit and the distance of the O atoms of the oxoanion) [16].

4. Conclusion

In summary, the anions receptor **2** based on the dihydrazones containing –NH binding sites of selectively sensing acetate ion has been synthesized and examined for its anions-binding abilities by UV–vis absorption spectroscopy. For all of the anions studied, only acetate ion is capable of changing the UV–vis intensity. It indicated that a strong binding interaction took place between the acetate ion and the receptor **2**. The receptor **2** also distributes a dramatic color change from yellow to green with the 2-acetate interaction. The receptor **1** has no abilities with all anions studied. That indicates the N–H fragment of a receptor can be further polarized, and its H-bond donor tendencies increased, through the insertion onto the molecular framework of electron-withdrawing substituents (e.g., $–NO_2$, CF_3). This investigation may represent a case study for the interaction of hydrazones with anions. Phenylhydrazones with an electron-withdrawing substituent is an appropriate receptor for acetate ion. It has a high selective binding ability for acetate while can distribute a dramatic color change with the host–guest interaction. This study indicates that the receptor **2** has latent application as a naked-eyes colorimetric sensor for acetate ion.

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