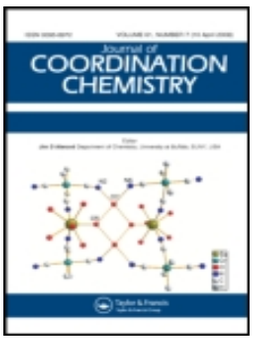

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Synthesis of an anion receptor for acetate based on the frame of ferrocene

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An anion receptor was synthesized with ferrocene as binding frame. Anion recognition can be monitored by anion complexation-induced changes in UV-vis absorption spectra. Interaction between the receptor and acetate was described on the basis of ^{1}H NMR experiments.

Keywords: Ferrocene; Phenylhydrazone; Receptor; Naked-eye recognition

1. Introduction

Anion recognition has attracted attention due to medicinal and environmental applications [1–3]. Receptors [4] and sensors [5–7] having strong affinity and selectivity for specific anions are important in supramolecular chemistry [8], but design of receptors with high selectivity is challenging [9–11]. Synthetic receptors for anions are usually based on urea/thiourea [12, 13], amides [14, 15], macrocyclic ammonium/guanidinium [16, 17], functionalized calixarenes [18, 19], and phenylhydrazone [20]. Phenylhydrazone, for example, is neutral and synthesis simple; *p*-nitrophenylhydrazine recognizes anions with a color change. The color of phenylhydrazone changed so obviously upon addition of anions that naked-eyed detection could be used. We found recently [21] that the phenylhydrazone-based indole receptor was effective for acetate in dry DMSO. Cheng *et al*. [22] showed that the pyrrole- and cystine-based cyclopeptido-mimetics bind fluoride and acetate ions in CH^3CN. BF^2 complexes of fluorinated dipyrrolyldiketone derivatives were also efficient receptors for acetate [23].

There are few reports on sensors for acetate based on 1,1′-diacetylferrocene; 1,1′-diacetylferrocene can provide an excellent frame for forming a geometrical cavity

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for a specific anion. In the present work, we designed and synthesized the receptor **1**, which senses acetate.

2. Results and discussion

2.1. *UV-vis spectroscopic measurement*

The UV-vis experiments of **1** with anions such as fluoride, chloride, bromide, iodide, dihydrogen phosphate, and acetate (tetrabutylammonium salts (TBA)) were carried out in DMSO at 298.2 ± 0.1 K. The anions were titrated into solution of **1**, which exhibited selective recognition for AcO^- as shown in figure 1. The UV-vis curves of **1** with different concentrations of acetate were studied (figure 2). The intensity of the absorption at 426 nm markedly decreased with simultaneous growth of a new peak at 585 nm as the anion concentration increased. The spectral changes of AcO^- are more obvious than F^- and $H_2PO_4^-$, but similar to OH^-. The presence of isobestic points at 475 nm during titration with acetate reveal formation of 1 : 1 complexes. No significant change in absorption was observed for Cl^-, Br^-, and I^-.

Continuous variation method was used to determine the stoichiometric ratios of the receptor to the fluoride guest. Figure 3 shows the receptor-AcO^- Job plot of the 585 nm band absorption *versus* the molar fraction of guest $\{[G]/([H]+[G])\}$ for a series of solutions in which the total concentration of the host and fluoride was constant (4.0×10^{-5} mol dm^{-3}), with the molar fraction of the guest continuously varying [24]. The result illustrates that the receptor-anion complex concentration approaches a maximum when the molar fraction of the host $\{[H]/([H]+[G])\}$ is about 0.50, meaning that the receptor forms a 1 : 1 complex with fluoride.

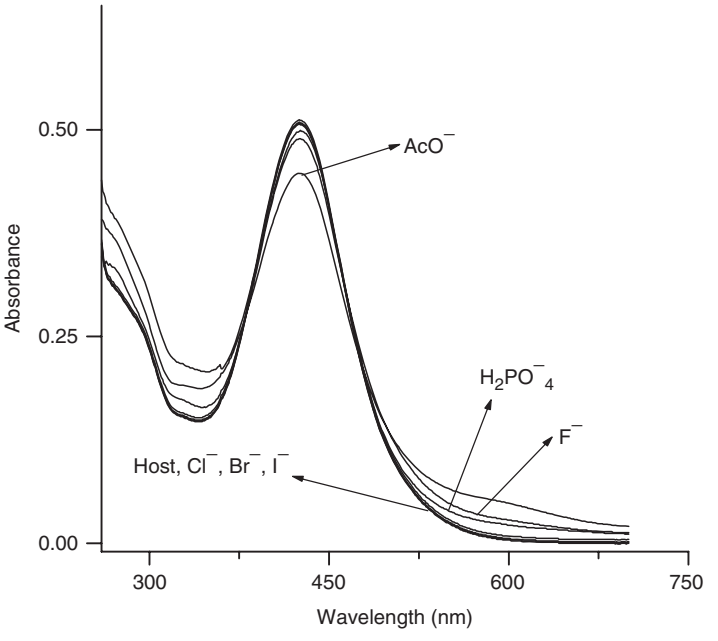


Figure 1. UV-vis changes of **1** operated in DMSO (1.0×10^{-5} M) after addition of two equivalent of anion.

For a complex of 1 : 1 stoichiometry, the relation in equation (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 [25].

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

Detailed data are given in table 1. The association constant K_{ass} was calculated by nonlinear least square regression [21]. The association constant for AcO^- was larger than that of OH^-, F^-, or $H_2PO_4^-$. The reason was probably that recognition of acetate is related to the configuration of acetate matching with the receptor (figure 1) and the basicity of acetate, as well as the acidity of the binding sites of receptor. The O–C–O angle is about 120°, with the distance of two oxygens fitting to the hydrogens on recognition points of receptor. Although the basicity of AcO^- is weaker than OH^-, its size matches the cavity better. Basicity of acetate is stronger than the other anions. Therefore, the association constant K_{ass} for acetate was maximal. The O–P–O angle is about 108° for $H_2PO_4^-$; the distance of two oxygen atoms of AcO^- is longer than that of $H_2PO_4^-$ such that oxygens of $H_2PO_4^-$ could not match well with two hydrogens on recognition sites. F^- has the smallest radius, but the better basicity gives a higher association constant K_{ass} than $H_2PO_4^-$. Table 1 shows the receptor binds anions in the order $AcO^- > OH^- > F^- > H_2PO_4^- > Cl^- \sim Br^- \sim I^-$.

2.2. *^{1}H NMR titrations*

Further support that formation of a hydrogen bond of N–H with anion came from ^{1}H NMR spectroscopic analyses. These were carried out in DMSO-d_6 under conditions of

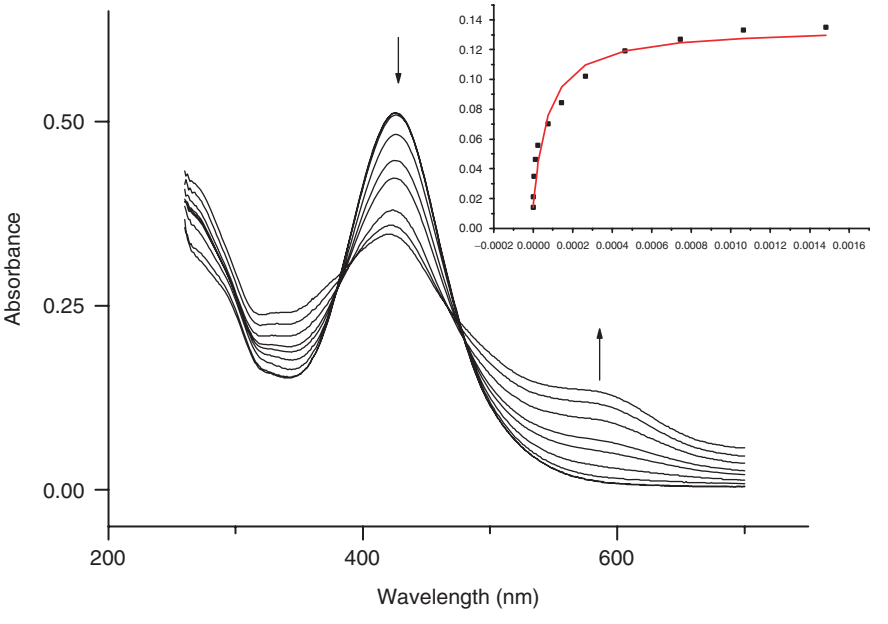


Figure 2. UV-vis spectra of **1** at 2×10^{-5} M in DMSO solution during titration with TBA acetate; the inset figure shows the nonline fitting profile of the receptor at 585 nm upon addition of TBA acetate.

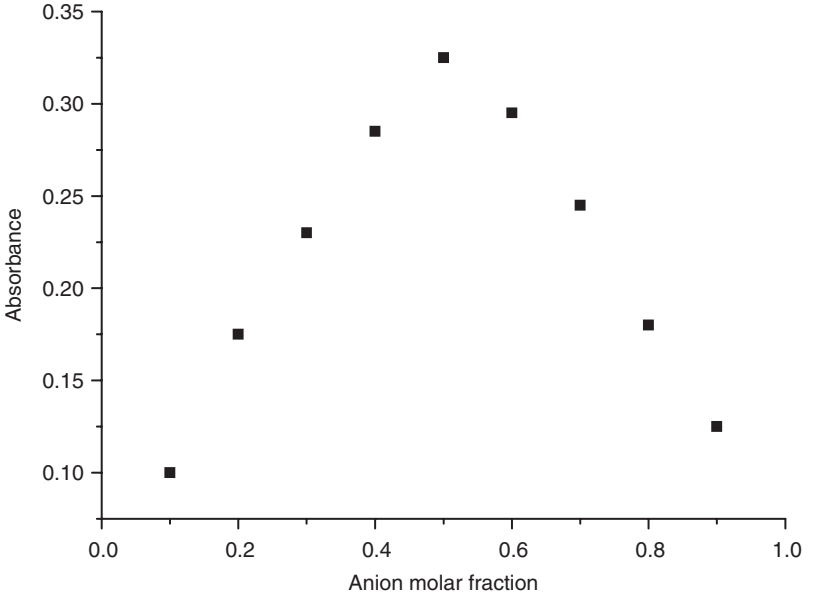


Figure 3. Job plot of **1** with AcO^-; total concentration is 4.0×10^{-5} M.

Table 1. Association constants, K_{ass}, of **1** with anions in DMSO at 298.2 ± 0.1 K.

Anion	AcO^-	OH^-	F^-	$H_2PO_4^-$	Cl^-	Br^-	I^-
K_{ass} (M^{-1})	3.91×10^4	9.8×10^3	4.3×10^3	1.6×10^3	ND	ND	ND

Note: The anions were added as their tetrabutylammonium salts. All errors are ±10%; ND: the spectra have too small change with adding anion to determine the affinity constant.

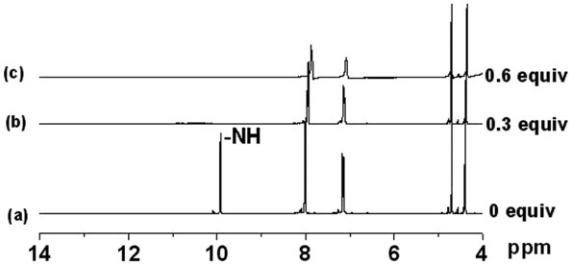
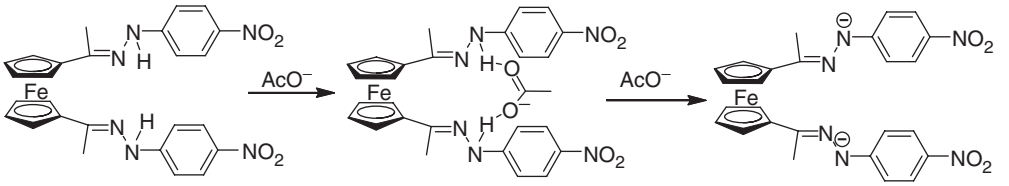
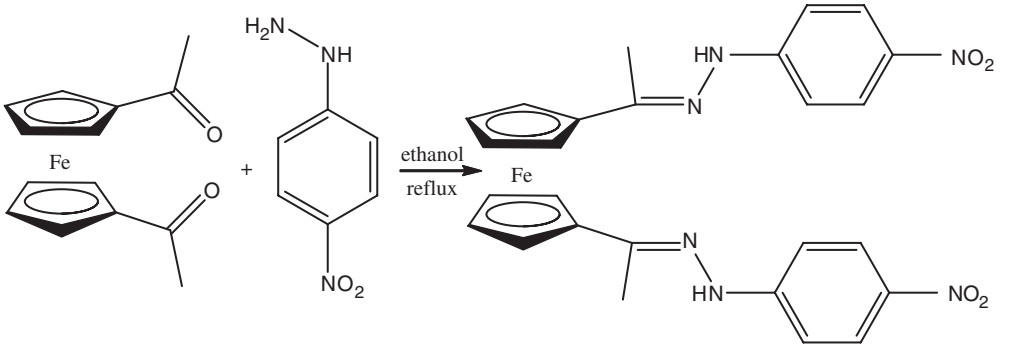


Figure 4. N–H ^{1}H NMR (400 MHz) spectra of **1** in DMSO-d_6 in the absence (a) and (b) the presence of 0.3 equivalent of AcO^- or 0.6 equivalent of AcO^- (c).

NMR titration, with the spectra of the receptors being recorded in the presence of increasing concentrations of anions (figure 4). Resonances corresponding to C–H of phenyl shift upfield during the titration, indicating increase of electron density on the phenyl ring from through-bond effects. Simultaneously, signals from the binding sites broadened with a downfield shift of 0.52 ppm upon addition of 0.3 equivalent of AcO^-,



Scheme 1. The proposed binding between **1** and acetate.



Scheme 2. The synthetic procedure for **1**.

and disappear when 0.6 equivalent of AcO^- was added, indicating complete deprotonation of **1**. The results indicate that there are two steps in anion recognition: (1) in the first step, acetate hydrogen bonds with **1**, and (2) deprotonation of **1** takes place. The proposed binding process between **1** and acetate is given in scheme 1.

3. Conclusion

Compound **1** has been developed as a colorimetric receptor for anions (scheme 2). The synthesis of this receptor is simple and high yielding. The receptor binds anions in 1 : 1 stoichiometry with obvious colorimetric changes; deprotonation is proved by ^1H NMR titration. The receptor has a selectivity for acetate and may have promising practical applications.

4. Experimental

4.1. *Reagents*

The tetrabutylammonium salts with different anions were purchased from Sigma-Aldrich Chemical Co., stored in a desiccator containing dry silica gel under vacuum, and used without purification. Solvents were purified and stored under nitrogen prior to use. DMSO was dried with calcium hydride and distilled at reduced pressure. Unless stated otherwise, commercial grade chemicals were used without purification.

4.2. *Synthesis of receptor 1, 1,1′-diacetylferrocene di-p-nitrophenylhydrazone*

A solution of 1,1′-diacetylferrocene (0.625 g, 2.5 mmol) in ethanol (20 mL) was added dropwise to a solution of *p*-nitrophenylhydrazine (0.765, 5 mmol) in ethanol (60 mL) with stirring at reflux. After stirring for 6 h, the solution was concentrated by evaporation. Recrystallization from ethanol yielded brown crystals. ^{1}H NMR δ (400 MHz, DMSO-d_6, Me_4Si): 9.9 (s, 2H, N–H), 8.1 (dd, 4H, Ar–H), 7.2 (dd, 4H, Ar–H), 4.7 (m, 4H, Fc), 4.4 (m, 4H, Fc), 1.0 (S, 6H, CH_3–H); ^{13}C NMR (DMSO): δ 151.2, 147.1, 137.8, 125.8, 111.5, 85.6, 70.5, 68.2, 67.7, 65.9, 64.1, 63.8, 39.6 ppm. Calcd for $C_{26}H_{26}FeN_6O_4$: C, 57.56; H, 4.79; N, 15.50. Found: C, 57.77; H, 4.68; N, 15.23. ESI-MS (m/z): 542.41$(M+H)^+$.

4.3. *General methods*

Unless otherwise specified, all UV-vis titration experiments were carried out at 298.2 ± 0.1 K. The ^{1}H NMR spectra were recorded on a Varian UNITY-plus 400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. UV-vis spectra were recorded on a Shimadzu UV-2450 PC spectrophotometer.

4.4. *Absorption titration studies*

Binding ability of the receptor for $CH_3CO_2^-$, $H_2PO_4^-$, and halide anions (as tetrabutylammonium salts) was investigated by UV-vis spectrometry in DMSO using a constant host concentration (2.0×10^{-5} M) and increasing concentrations of the anions (0–12 equivalence). The change in absorbance at 584 nm for the receptor was plotted against anion concentration and fitted by the equation described by Connors [24].

4.5. *^{1}H NMR titrations*

The receptor (5.0×10^{-3} M in DMSO-d_6) was titrated against acetate (tetrabutylammonium salts) by addition of excess anion in DMSO-d_6.

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