Research Article

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Study on optical recognition and electrochemical sensing of a 1,1′-ferrocenedicarbonylhydrazine derivative for fluoride

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A new compound, 1,1′-di-(*p*-nitrophenylhydrazino-*β*-carbonyl)-ferrocene (1) was designed as an anion receptor based on its hydrogen bonding interaction with anions. Investigation of UV–vis spectra showed that it was an excellent optical sensors for F^-. Furthermore, the nature of interaction between it and F^- was investigated by ^1H NMR titration experiments. In addition, the efficiency of the receptor applied as an electrochemical sensor for F^- was discussed by cyclic voltammetry (CV). **Copyright © 2008 John Wiley & Sons, Ltd.**

Keywords: anion recognition; electrochemical sensor; selectivity; ferrocene; naked-eye detection

Introduction

Increased understanding of the environment, industrial and biological processes has led to increased research into anion-selected recognition and sensing.[1–4] It is also important to design and synthesize sensitive receptors for certain biologically important anions like fluoride, acetate, dihydrogenphosphate, chloride, bromine and iodine.[5] The receptors containing urea,[6] thiourea,[7] amide,[8] pyrrole,[9] imidazole[10] and phenol[11] subunits have been well investigated and present excellent selectivity. Recently, the carbonylhydrazine derivatives have attracted considerable attention as they function as selective anion sensors. Evans *et al*. synthesized a series of compounds developed by pyrrole carbonylhydrazine and investigated their anion-binding properties.[12] Also, Quinlan *et al*. showed that receptors based on calix[4]arene carbonylhydrazine behaved as excellent sensors of fluoride.[13] Similarly, 'naked-eye' detection receptors for fluoride and pyrophosphate developed from calix[4]arene carbonylhydrazine were reported by Quinlan *et al*.[14]

From these achievements, we learn that, despite these receptors being reported, there have been few studies on receptors combining the redox units and the carbonylhydrazine units. The ferrocene moiety has been studied extensively in the redox-responsive anion receptors, since it offers the possibility to modulate anion–receptor interactions according to the redox state; e.g. electrostatic interactions can be switched on by the oxidation of ferrocene to ferricinium.[15] In addition, we have recently reported the anion receptors based on ferrocene sensing of a $H_2PO_4^-$ well.[16]

In this paper, we designed and synthesized the receptor by combining the redox activity of the ferrocene moiety with *p*-nitrophenylhydrazine (Scheme 1). The investigation of the receptor showed that it is an excellent sensor for F^-. In particular, the receptor displayed highly selective UV–vis spectra changes with F^- among the various anions we studied. Furthermore, the nature of the interaction between the receptor and the F^- was investigated by ^1H NMR titration experiments. Additionally, the cyclic voltammetry experiments bestowed as consistent a result as UV–vis investigation, which should be of interest for future applications of F^- sensors (Scheme 1).

Experimental Section

Apparatus

^1H NMR spectra were obtained on a Varian UNITY Plus-400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. Electrochemical measurements were performed using a CH-Instruments-430 potentiostat interfaced with Pentium PC. SI-MS was performed using a Mariner apparatus. C, H, N elemental analyses were made on an elementar vario EL. UV–vis spectra were recorded on a Shimadzu UV2450 spectrophotometer with a quartz cuvette (path length = 1 cm).

Reagents

Unless otherwise specified, all reagents for synthesis were obtained commercially and were used without further purification. In the titration experiments, all the anions were added in the form of tetra-*n*-butylammonium (TBA) salts, which were purchased from Sigma-Aldrich Chemical, stored in a vacuum desiccator containing self-indicating silica and fully dried before using. DMSO was dried with CaH_2 and then distilled in reduced pressure.

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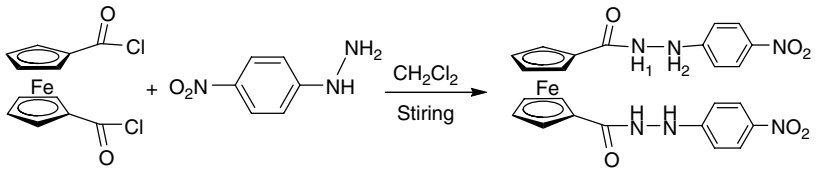

Scheme 1. The synthetic route of the receptors of **1**.

General method

All experiments were carried out at 298 K, unless otherwise mentioned. UV–vis spectra were measured using an ultraviolet–visible spectrophotometer, UV-2450 (Shimadzu Corp., Kyoto, Japan). A 2.0×10^{-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^{-2} M tetrabutyl ammonium (TBA) salts of the respective anions were prepared in dried and distilled DMSO and were stored under a dry atmosphere.

^{1}H NMR titration experiments were carried out in DMSO-d_6 solution (TMS as the internal standard). A 1.5 mg aliquot of receptor **1** was dissolved in DMSO-d_6 to a concentration of 2×10^{-4} M. Then an increased amount of fluoride anion (in DMSO-d_6) was added to the solution, and ^{1}H NMR of the host–guest system performed.

Electrochemical measurements were performed in CH_3CN solution (dried with CaH_2). A platinum wire was used as an auxiliary electrode, an Ag–AgCl reference electrode was used and the working electrode was a glassy carbon electrode (diameter = 3.8 mm). $NaClO_4$ (0.1 mol/l) was present as the supporting electrolyte. The scan rate was 100 mV/s.

Synthesis of 1,1′-di-(*p*-nitrophenylhydrazinocarbonyl)-ferrocene (1)[17]

A solution of 1,1′-ferrocenyldicarbonyl dichloride (0.78 g, 2.50 mmol) in CH_2Cl_2 (30 ml) was added slowly at 0 °C to a solution of (4-nitrophenyl)hydrazine (0.765 g, 5.00 mmol) and pyridine (0.4 ml, 5.00 mmol) in CH_2Cl_2 (20 ml). The reaction mixture was stirred for 12 h, and the precipitate formed was filtered off and washed five times with CH_2Cl_2 (30 ml). This procedure yielded 0.99 g (72%) of pure product after drying *in vacuo*. ^{1}H NMR(400 MHz; DMSO-d_6; Me_4Si): 10.1 (2H, s, CONH), 9.2 (2H, s, NH), 8.1 (4H, d, Ph), 6.9 (4H, d, Ph), 5.0 (4H, s, Fc), 4.6 (4H, s, Fc). Elemental analysis: calcd for $C_{24}H_{20}FeN_6O_6$: C, 52.94; H, 3.68; N, 15.44; found: C, 53.25; H, 3.27; N, 15.53. ESI-MS (*m/z*): 544.41(M + H, calcd 544).

Results and Discussion

UV–Vis spectroscopy

First, to evaluate the templating ability of anions, the UV–vis titration experiments of the receptor **1** were carried out in dry DMSO solution using standard tetrabutylammonium salts of AcO^-, F^-, $H_2PO_4^-$, Cl^-, Br^- and I^- at 298.2 ± 0.1 K. The UV–vis spectrum of the solution of **1** (1.0×10^{-5} M) was recorded upon the addition of F^- (see Fig. 1). In the absence of the anion, an absorption maximum was seen at 380 nm. Upon the addition of F^-, a red shift at 394 nm was observed ($\Delta\lambda = 14$ nm) while a new peak at 520 nm formed gradually. Similarly, the addition of AcO^- and $H_2PO_4^-$ also led to spectral changes, but the changes were smaller. However, as the Cl^-, Br^- and I^- were titrated into **1**, the spectra hardly changed even when the anions were excessive. the continuous variation method was used to determine the stoichiometric ratios of the receptors to the fluoride anion guest. In Fig. 2 a job plot[18,19] of receptor **1** and F^- in DMSO shows the maximum at a molar fraction of 0.5. This result indicates that the receptor **1** binds fluoride anion guest with a 1 : 1 ratio. Moreover, similar results can also be obtained for other anions (AcO^- and $H_2PO_4^-$).

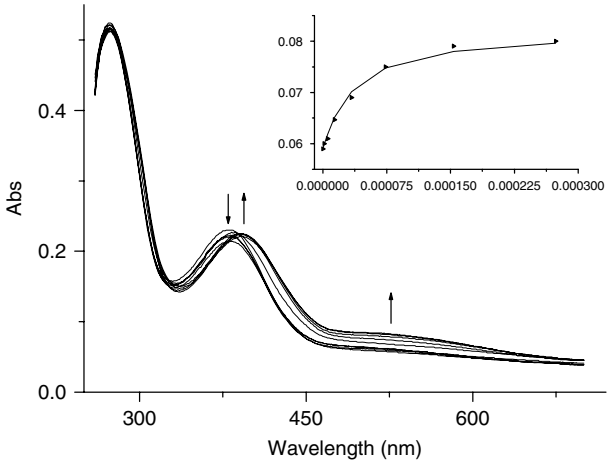

Figure 1. Family of spectra taken in the course of the titration of a 1.0×10^{-5} M solution of **1** with a standard solution of F^- at 298.2 ± 0.1 K.

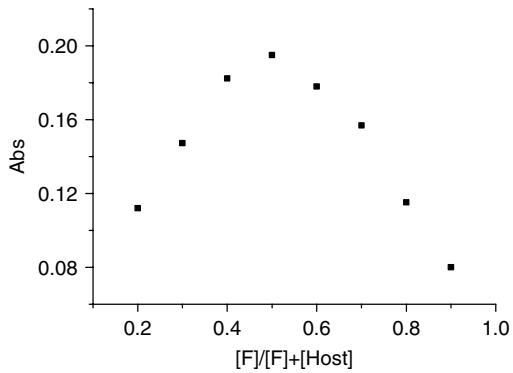

Figure 2. A job plot for complexation of receptor **1** with F^- determined by UV–vis in DMSO at 298.2 ± 0.1 K, $[\mathbf{1}] + [F^-] = 2.0 \times 10^{-5}$ M.

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.[20]

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

The affinity constants of receptors **1** and **2** for anionic species were calculated and are listed in Table 1. Obviously, the recognition

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Table 1. The affinity constants of receptors **1** and **2** with anions at 298.2 ± 0.1 K in DMSO

	AcO^-	F^-	$H_2PO_4^-$	Cl^-	Br^-	I^-
log $K_{S,1}$	2.51 ± 0.12	3.92 ± 0.25	2.44 ± 0.14	ND	ND	ND

ND, cannot be determined.

Figure 3. Color changes of **1** (5.0×10^{-5} M) upon addition of 3 equiv of different anions in DMSO at 298 K (from left to right: **1** only, **1** + F^-, **1** + AcO^-, **1** + $H_2PO_4^-$, **1** + Cl^-, **1** + Br^-, **1** + I^-).

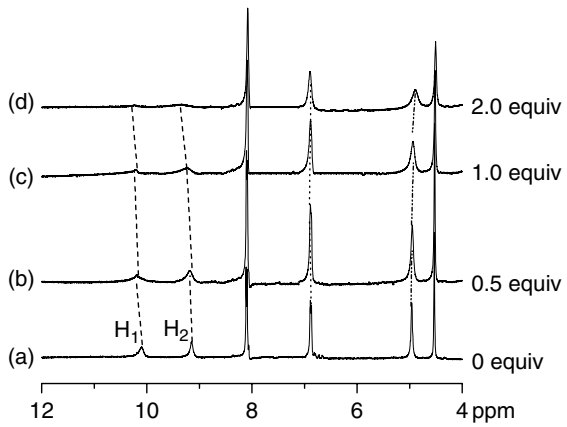


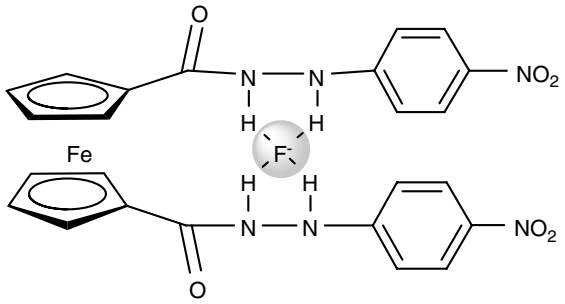
Figure 4. N–H ^{1}H NMR (400 MHz) spectra of **1** in DMSO-d_6: the absence (a) and the presence of (b) 0.5, (c) 1.0 and (d) 2.0 equiv of F^-.

function of **1** for F^- is the most remarkable property. The reason may be that receptor **1** has the correct cavity for F^-, which is a spherical anion that can geometrically match the receptor better than trigonal or tetrahedral anions. Furthermore, F^- is an atom anion, which means that it can form a five-membered chelate ring with the carbonylhydrazine derivatives that is steadier than the seven-membered chelate ring formed by AcO^- or $H_2PO_4^-$. Finally, the ability of F^- to bind H is much stronger than that of Cl^-, Br^- and I^-.

As a validation to the titration experiments, 'naked-eye' detection experiments were performed. Visual inspection of a solution of **1** after addition of varies tetrabutylammonium (TBA) anions showed a dramatic change, from brown to purple, in the case of F^-, suggesting strong binding, whereas the addition of AcO^- or $H_2PO_4^-$ resulted in a lesser change in color and Cl^-, Br^- or I^- even brought on almost no change of color (see Fig. 3).

^{1}H NMR spectroscopic experiments

Proton NMR titration experiments were conducted to further investigate the interaction of **1** with F^- in DMSO-d_6. As shown in Fig. 4, upon addition of F^- to the solution of **1**, the original peaks of H_1 and H_2 (marked in Scheme 1) appeared at 10.14 and 9.10 ppm, respectively, shift downfield. When 2 equiv F^- were added to **1,** their peaks broadened and moved downfield to 10.35 ppm ($\Delta\delta$ = 0.21 ppm) and 9.43 ppm ($\Delta\delta$ = 0.33 ppm), respectively.



Scheme 2. The proposed binding mode of **1** and F^-.

Table 2. Electrochemical response of receptor 1 to anionic guests

Anion	AcO^-	F^-	$H_2PO_4^-$	Cl^-	Br^-	I^-
$\Delta E_{pa,1}$ [a] (mV)	34	97	38	– [b]	– [b]	– [b]

[a] Anode shift of the oxidation wave of receptor **1** with 3 equiv of anionic guest added in DMSO solution; solutions were 2.0×10^{-3} M in receptor, temperature = 298 K, $\Delta E_{pa,1} = E_{pa,1} - E_{pa,1+anion}$; [b] too small to be determined.

This suggests that F^- is being combined with the receptor **1** by hydrogen bondings. Furthermore, the signals of H at the phenyl ring fragment shifted upfield, owing to the electron density in the phenyl fragment being increased by the formation of a complex between the receptor **1** and F^-. In addition, we show the possible binding model of the receptor **1** and F^- interaction in Scheme 2.

Electrochemistry experiments

In order to exploit the potential electrochemical sensing capability of the receptor **1** with the incorporation of a redox center proximate to the anion-binding site, the chemical behavior of the sensor was investigated by cyclic voltammetry (CV) in acetonitrile containing 0.1 M $NaClO_4$ as supporting electrolyte.

Figure 5 shows the CVs of receptor **1** operated in acetonitrile (2.0×10^{-3} M) after the addition of 3 equiv of F^-, AcO^- and Cl^-. From Fig. 5, the CVs of **1** change the most drastically upon the addition of 3 equiv of F^-. Similarly, the addition of the same concentrations of F^-, AcO^- and $H_2PO_4^-$ caused a significant electrochemical response in that the oxidation wave moved to more negative potentials, whereas F^- behaved the best of the three, with the $\Delta E_{pa,1}$ = 97 mV (see Table 2). All these results show that the anions have been coordinated to the –NH protons close to the ferrocene group, which facilitates the redox process.

Summary

In summary, we have successfully studied the designed receptor based on ferrocene. UV–vis spectral titration experiments showed that the receptor from 1 : 1 stoichiometric complexes in DMSO solution is an excellent sensor for F^-. Also, naked-eye detection gaved a differentiation of F^- among the anions investigated. Proton NMR anionic titration showed that the receptors combine F^- by hydrogen bonding. Furthermore, electrochemical investigation revealed that the receptor had great potential for the development of novel electrochemical sensory devices. We believe that

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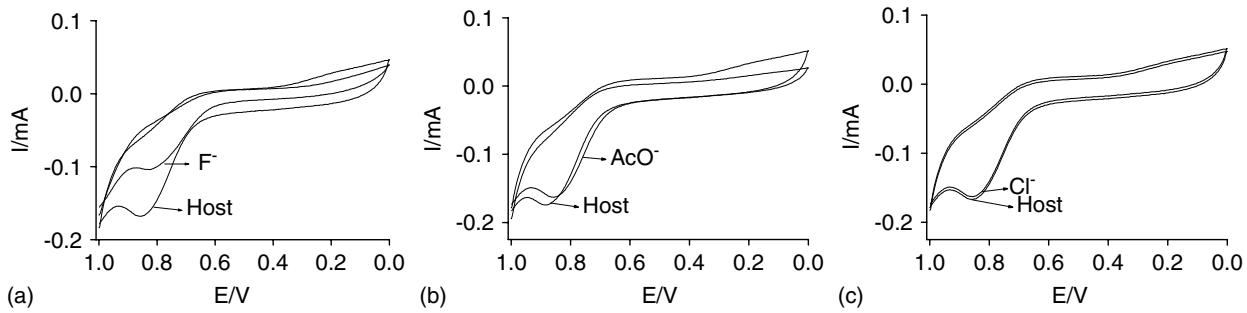

Figure 5. (a) CVs of receptor **1** operated in acetonitrile (2.0×10^{-3} M) after the addition of 3 equiv of F^-; (b) CVs of receptor **1** operated in acetonitrile (2.0×10^{-3} M) after the addition of 3 equiv of AcO^-; (c) CVs of receptor **1** operated in acetonitrile (2.0×10^{-3} M) after the addition of 3 equiv of Cl^-.

the results presented will be useful for the design of a more sensitive receptor for F^- optically and electrochemically.

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