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Ferrocene-based imidazolium receptors for anions

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ABSTRACT

Cyclic and acyclic ferrocene derivatives bearing two imidazolium rings have been synthesized and characterized by NMR, elemental analysis, mass spectra, and X-ray crystallography. Electrochemical measurements revealed that all the receptors displayed a significant anodic shift response for F^-. In addition, for receptors **1**, **2**, and **4**, addition of HSO_4^- induced quite different electrochemical behavior with dramatic cathodic peak current increase on CV. ^1H NMR titrations demonstrated that receptors **1**, **2**, and **4** showed selectivity for AcO^- while receptor **3** exhibited high affinity toward Cl^- among the anions investigated.

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1. Introduction

Anions play a fundamental role in a wide range in biology, medicine, catalysis, and the environment.[1] Considerable attention has been paid to the design and synthesis of abiotic receptors for anionic species in the past two decades, which make anion recognition one of the fastest growing disciplines in the field of supramolecular chemistry.[2] In recent years, the development of chemsensors capable of selectively recognizing and sensing anions appears to be particularly attractive owing to their simplicity and convenience.

The imidazolium group is an attractive building block for anion receptors because it contributes one relatively strong hydrogen-bonding site. Unlike those most commonly utilized anion binding groups such as neutral (thio)urea, pyrrole, and amide, which form N–H···X^- hydrogen bonds and positive charged ammonium or guanidinium groups involving N^+–H···X^- hydrogen bonds, imidazolium group can interact with anions through (C–H)$^+$···X^- type ionic hydrogen bonds.[3] Recently, numerous efforts have been devoted to the study of imidazolium derivatives as anion receptors.[4] Kim et al. have done excellent work.[5] They have investigated a lot of imidazolium bearing receptors including tripodal nitro-imidazolium receptor,[5a] calix-imidazolium system[5e] and fluorescent imidazolium systems,[5d,f] etc. More recently, Pandey et al. utilized deoxycholic acid as scaffold to design novel imidazolium-containing receptors.[6] Fabbrizzi et al. reported a metal-based trisimidazolium cage, which can include diverse anions via six hydrogen bonds.[7]

A number of imidazolium-based receptors and fluorescent sensors have been reported in the last several years. But it seems rather rare for sensors utilizing both redox-active groups and imidazolium rings,[8] especially for cyclic ones.[8c] In order to expand this area and investigate how structure of the receptors will influence the binding affinity and selectivity, we synthesized a series of cyclic and acyclic imidazolium-based receptors **1**–**4** and studied their recognition properties toward various anions (Fig. 1).

2. Results and discussion

2.1. Synthesis

The synthetic procedure of compounds **1**–**4** is summarized in Scheme 1. All the receptors were synthesized starting from 1,1′-bis(hydroxymethyl)ferrocene **5**, which was obtained from the literature method.[9] By reacting with phosphorus tribromide or *N*,*N*′-carbonyldiimidazole (CDI), compound **5** was converted to two

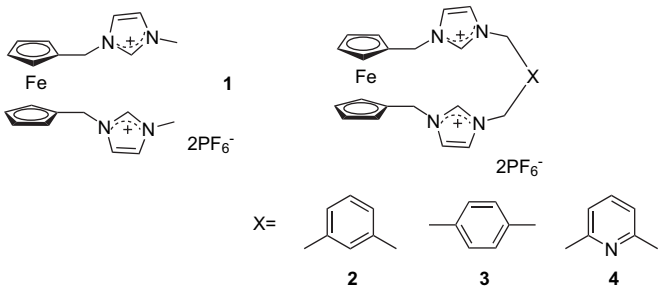

Figure 1. Structures of electrochemical sensors **1**–**4**.

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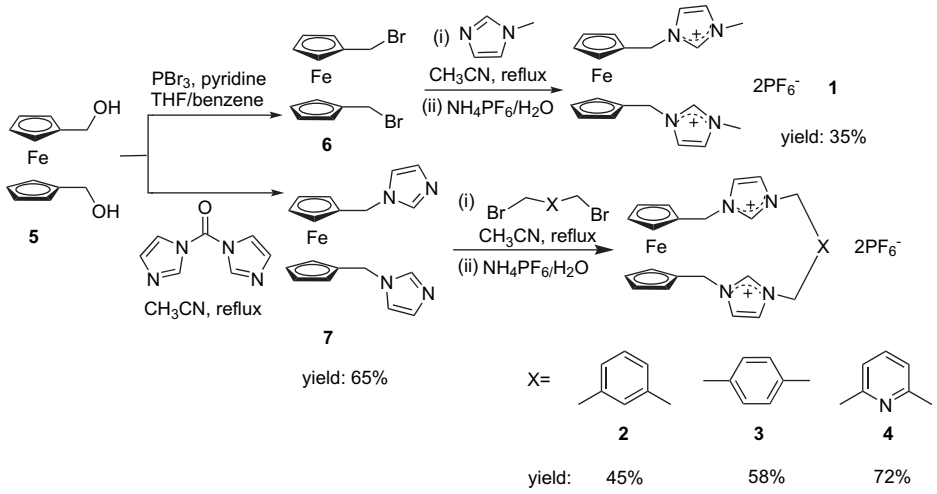

Scheme 1. Synthetic procedure of receptors **1**–**4**.

important precursors 1,1′-bis(bromomethyl)ferrocene **6**[10] or 1,1′-bis(imidazolylmethyl)ferrocene **7**.[11] Receptor **1** was synthesized by the reaction of compound **6** and 1-methylimidazole in CH_3CN overnight. The solvent was evaporated to dryness. The residue was dissolved in water and a saturated solution of NH_4PF_6 was added dropwise to get compound **1** as yellow precipitate. The receptors **2**–**4** were synthesized under high dilution conditions by the reaction of 1,1′-bis(imidazolylmethyl)ferrocene **7** with *m*-xylylene dibromide, *p*-xylylene dibromide, and 2,6-bis(bromomethyl)pyridine to give receptors **2**–**4**, respectively, after the same work up as that of **1**.

The crystals of **1**·2(PF_6^-), **2**·2(PF_6^-), and **4**·2(PF_6^-) were obtained by slow diffusion of petroleum ether into the acetone solution of them. Crystal of **3**·2(PF_6^-) was obtained by slow diffusion of petroleum ether into the mixture solution of **3**·2(PF_6^-) in acetone and acetonitrile while crystal of **1**·2(Br^-) was obtained by diffusion of ether into the methanol solution of **1**·2(Br^-). The structures of all the crystals are illustrated in Figure 2.

2.2. Crystal structures

In the solid state, two methyl imidazolium groups of **1**·2(PF_6^-) and **1**·2(Br^-) adopt a 'trans' conformation with respect to the ferrocene moiety. In the case of **1**·2(PF_6^-), two PF_6^- anions form hydrogen bonds with C-3 proton of the ferrocene and C-5 proton of the imidazolium ring, respectively, while for **1**·2(Br^-), each of Br^- anions forms two hydrogen bonds with C-2 proton of the imidazolium ring and the methylene proton. The hydrogen-bonding distances and angles[12] are F(11A)···H(13A)=2.556 Å, ∠(C(13A)–H(13A)–F(11A))=174.1°, F(6CA)···H(8AA)=2.370 Å, ∠(C(8NA)–H(8AA)–F(6CA))=159.9°, Br(1A)···H(9B)=2.769 Å, ∠(C(9A)–H(9B)–Br(1A))=146.2°, Br(1A)···H(6AB)=2.894 Å, ∠(C(6B)–H(6AB)–Br(1A))=154.5°.

The structures of **2**·2(PF_6^-), **3**·2(PF_6^-), and **4**·2(PF_6^-) show different features in the solid state. In the crystal structure of **2**·2(PF_6^-), one PF_6^- is located on top of the macrocycle and interacts with the receptor through C(18A)–H(18A)···F(11A) hydrogen bonding. The other PF_6^- is located at the side of the receptor. There is an intramolecular hydrogen bond between the N(3) and the H(16A). In the structure of **3**·2(PF_6^-), two negative anions are located on top and at the bottom of the cavity. Both of them are coordinated to the methylene proton between the ferrocene unit and the imidazolium ring. In contrast to **2**·2(PF_6^-) and **3**·2(PF_6^-), for **4**·2(PF_6^-), both of the two PF_6^- anions are located at the side of the macrocycle. The hydrogen-bonding distances and angles[12] are F(4A)···H(12A)=2.526 Å, ∠(C(12A)–H(12A)–F(4A))=162.5°, F(11A)···H(18A)=2.456 Å, ∠(C(18A)–H(18A)–F(11A))=123.0°, F(4AA)···H(6AA)=F(4AB)···H(6AB)=2.530 Å, ∠(C(6AA)–H(6AA)–F(4AA))=∠(C(6AB)–H(6AB)–F(4AB))=136.0°, F(1)···H(19)=2.323 Å, ∠(C(19)–H(19)–F(1))=176.0°, F(3)···H(23)=2.522 Å, ∠(C(23)–H(23)–F(3))=134.7°, F(10)···H(14)=2.497 Å, ∠(C(14)–H(14)–F(10))=136.7°.

2.3. Anion binding properties

2.3.1. Electrochemical studies

The electrochemical properties of receptors **1**–**4** (5×10^{-4} M) were investigated by cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) in CH_3CN solutions containing 0.1 M (n-Bu)$_4$NPF$_6$ as supporting electrolyte. The electrochemical behavior of the receptors alone and in the presence of various concentrations of anions (F^-, Cl^-, Br^-, I^-, AcO^-, and HSO_4^-) was studied. In the absence of anions, each free receptor exhibited a reversible one-electron redox wave (Fig. 3), typical of ferrocene derivatives. Compared to unsubstituted ferrocene, $E_{1/2}$s for **1**–**4** are shifted to more positive potentials (312–332 mV vs Fc^+/Fc) due to the electron-withdrawing effect of the imidazolium groups.

Due to the poor reversibility of the redox process when anions were added in the CV experiment, to make a good estimation about the $E_{1/2}$ values, OSWV technique was employed to obtain well-resolved potential information. The resulting E_p calculated values versus the ferrocenium/ferrocene (Fc^+/Fc) redox couple are listed in Table 1.

As can be seen from Figure 4a, addition of different anions to the CH_3CN solutions of **1**–**4** caused distinct behavior (also see Supplementary data) *on OSWV*. Remarkable responses were observed when F^- was added. For example, in the case of receptor **1**, ΔE_p=−284 mV versus Fc^+/Fc for fluoride while for receptor **4**, ΔE_p=−214 mV versus Fc^+/Fc, though smaller than that of **1**–**3**, still more than 200 mV. In contrast, addition of AcO^- only induced moderate changes of the E_p values, the most obvious was caused for **3**, ΔE_p=−152 mV versus Fc^+/Fc. Addition of other anions such as HSO_4^-, Cl^-, and Br^- had relatively weak interaction with the redox center and the changes in the E_p values were less than 100 mV while addition of I^- had no effect on the CV and OSWV of these receptors, even when present in large excess. It is noteworthy that addition of HSO_4^- exhibited some different behavior on CV. Unlike the other anions, addition of HSO_4^- to the CH_3CN solutions of receptors **1**, **2**, and **4** induced dramatic cathodic peak current increase (Fig. 4b and Supplementary data), which may be ascribed to

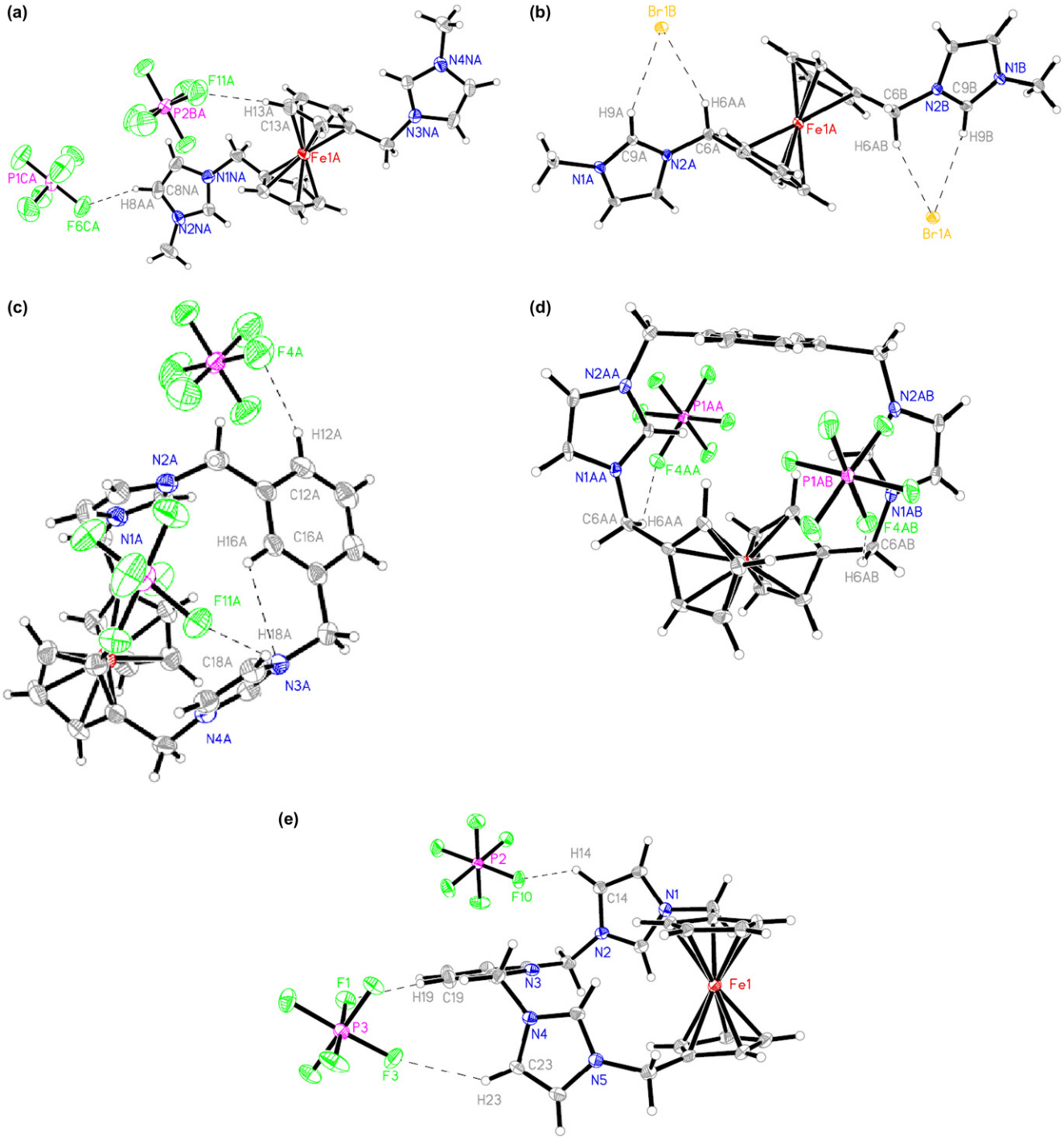

Figure 2. Crystal structures of (a) **1**·2(PF_6^-), (b) **1**·2(Br^-), (c) **2**·2(PF_6^-), (d) **3**·2(PF_6^-), and (e) **4**·2(PF_6^-) (thermal ellipsoids were set at 30% probability).

consumption of the receptors in a reduction reaction, possibly hydrogenation at the iron center.[8a,b]

2.3.2. *^{1}H NMR studies*

To gain more insight into the anion recognition properties of these receptors, ^{1}H NMR titration experiments were carried out by addition of the anions (Cl^-, Br^-, I^-, and AcO^-) as their tetrabutylammonium salts to CD_3CN solution containing hosts (5×10^{-3} M). The binding constants for F^- were not determined due to precipitation during the ^{1}H NMR titration. Upon addition of anions, significant downfield shifts (for receptors **1**–**4**, $\Delta\delta$ >1.9 ppm on addition of AcO^-) were observed for the C-2 proton of the imidazolium moieties, suggesting complexation of the anion by CH hydrogen bonds. The titration curves produced by monitoring the C-2 proton of the imidazolium units suggest 1:1 stoichiometry and the Job plot method clearly show this (Fig. 6b). The association constants of receptors **1**–**4** toward various anions tested were determined were determined by using a nonlinear curve fitting program[13] with results collected in Table 2.

From ^{1}H NMR it is observed that upon addition of anions, there were three kinds of protons showing obvious downfield shifts for receptor **1** (Fig. 5), i.e., the C-2 proton of the imidazolium ring (H_a),

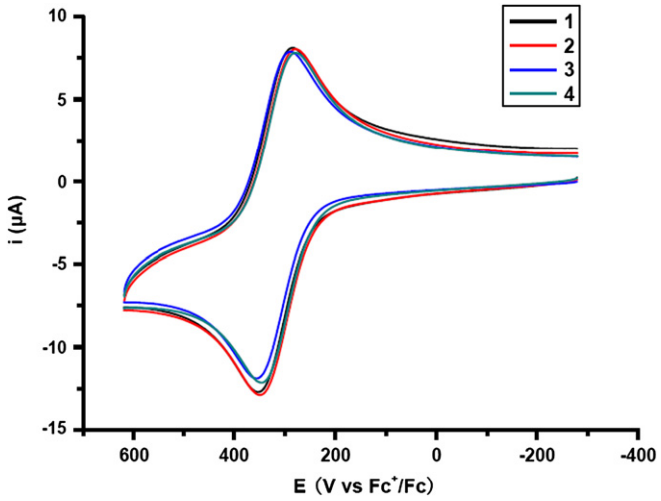

Figure 3. CV response of free receptors **1**–**4** (5×10^{-4} M) in CH_3CN; supporting electrolyte: 0.1 M $(n\text{-Bu})_4NPF_6$; scan rate: 100 mV/s.

C-5 proton of the imidazolium ring (H_b), and the methylene proton (H_c). The downfield shifts of the three kinds of protons indicated the presence of three main interactions between the receptor **1** and the anions in solution. From Table 2, we can see that receptor **1** displays selectivity for AcO^- over other anions in the order $AcO^->Cl^->Br^->I^-$, which is consistent with the electrochemical results. The trend can be ascribed to the basicity of these anions. We can also see that receptor **1** binds anions much less effectively than receptors **2**–**4** due to the poorer pre-organization of the acyclic receptor than the cyclic ones.

In the case of receptor **2**, the C-2 proton of the imidazolium ring (H_d) and one proton of the benzene ring (H_e) showed distinct downfield shifts (Fig. 6). For example, addition of 1 equiv of AcO^- induced $\Delta\delta$=2.03 and 1.17 ppm for H_d and H_e, respectively. So receptor **2** can bind anions mainly through two $(C\text{–}H)^+\cdots X^-$ type ionic hydrogen bonds and one $C\text{–}H\cdots X^-$ hydrogen bond provided by the benzene ring. Receptor **2** shows similar selectivity for anions as receptor **1** owing to the same reason.

Figure 7 shows the ^1H NMR spectra of receptor **3** before and after the addition of 1 equiv of Cl^-. Obvious downfield shifts were observed for three kinds of protons, i.e., the C-2 proton of the imidazolium ring (H_f), the methylene proton between the imidazolium ring and the ferrocene ring (H_g), and the C-2 proton of the ferrocene unit (H_h). Receptor **3** shows higher binding constants for halide anions compared to the other receptors, which may be ascribed to its larger cavity size and better pre-organization than the acyclic receptor **1**.

Similar downfield shifts were observed for receptor **4** (Fig. 8). The imidazolium C-2 proton (H_i) and the methylene proton between the imidazolium ring and the ferrocene ring (H_j) participated in the host–guest complexation process. Receptor **4** exhibits similar selectivity as receptors **1** and **2**, but the binding constants are much lower than receptor **2**. This may be ascribed to lone pair electrons on nitrogen, which prevents the anions from binding properly.[6c]

Table 1
ΔE_p[a] values associated with the complexing processes between the free receptors and the appropriate anion

Compd	R[b]	R·F^-	R·AcO^-	R·HSO_4^-[c]	R·Cl^-	R·Br^-
1	332	−284	−96	−28	−24	−16
2	320	−272	−108	−72	−40	−8
3	320	−276	−152	−28	−60	−16
4	316	−214	−116	−64	−28	−8

[a] In millivolt, obtained from the OSWV experiments carried out in CH_3CN; anions added as their tetrabutylammonium salts.
[b] E_p values corresponding to the free receptors.
[c] HSO_4^- (2.5 equiv) was added.

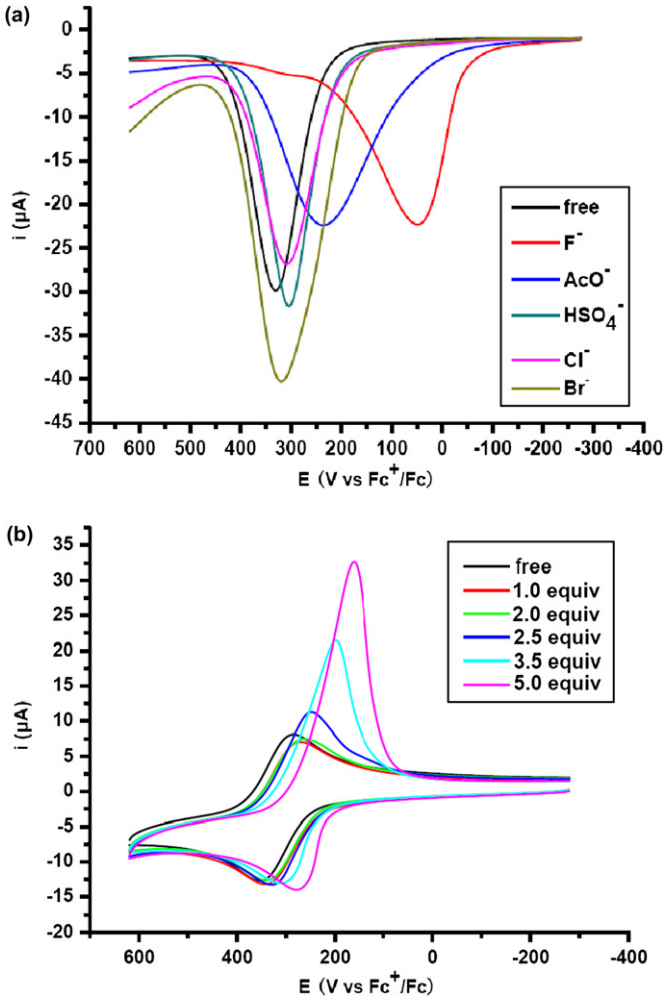

Figure 4. (a) Evolution of the OSWV of receptor **1** in CH_3CN upon addition of various anions, (b) CV of receptor **1** in CH_3CN on addition of various concentrations of HSO_4^-; supporting electrolyte: 0.1 M $(n\text{-Bu})_4NPF_6$; scan rate: 100 mV/s.

Table 2
Association constants (K_a) and binding free energies (ΔG^0) for 1:1 complexes of receptors **1**–**4** with anions in CD_3CN at 298 K[a]

Receptor	Anion[b]	K_a (M^{-1})	$-\Delta G^0_{298}$ (KJ mol^{-1})
1	AcO^-	9.8×10^2	17.1
	Cl^-	6.6×10^2	16.1
	Br^-	5.3×10^2	15.5
	I^-	2.2×10^2	13.4
2	AcO^-	2.3×10^4	24.9
	Cl^-	6.2×10^3	21.6
	Br^-	1.8×10^3	18.5
	I^-	3.6×10^2	14.6
3	AcO^-	1.9×10^4	24.4
	Cl^-	4.8×10^4	26.7
	Br^-	5.4×10^3	21.3
	I^-	7.1×10^2	16.3
4	AcO^-	4.2×10^3	20.7
	Cl^-	3.2×10^3	20.0
	Br^-	1.2×10^3	17.5
	I^-	2.9×10^3	19.8

[a] Errors are estimated to be <15%.
[b] Anions used as their TBA^+ salts.

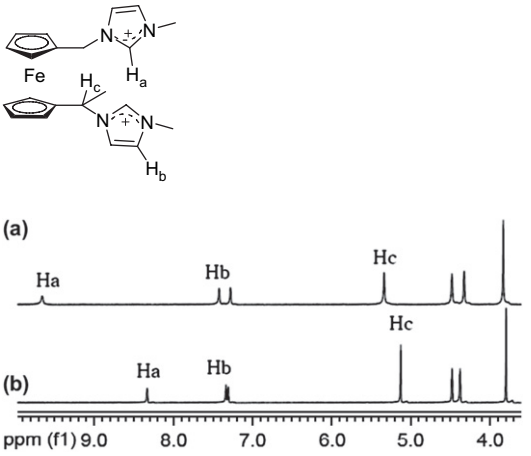

Figure 5. ^{1}H NMR spectra of host **1** before (b) and after (a) the addition of 1 equiv of AcO^- anion in CD_3CN.

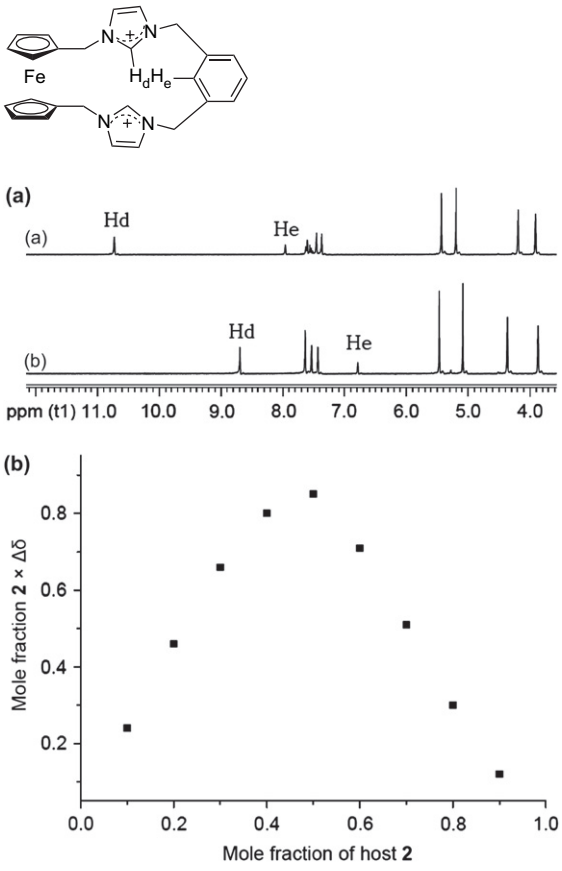

Figure 6. (a) ^{1}H NMR spectra of host **2** before (b) and after (a) the addition of 1 equiv of AcO^- anion in CD_3CN. (b) Job plot of host **2** with AcO^-.

3. Conclusion

A series of acyclic and cyclic ferrocene-based imidazolium receptors for anions were synthesized. Their anion binding properties were studied by utilizing electrochemistry, X-ray diffractometer analysis, and ^{1}H NMR titration experiments. All the receptors show effective electrochemical response for F^- with anodic shifts more than 200 mV. Dramatic cathodic peak current increase was observed upon addition of HSO_4^- to receptors **1**, **2**, and **4**, which can be used to discriminate HSO_4^- from the other anions. ^{1}H NMR analysis reveals that selectivity order and binding affinity for anions can be tuned by changing the pre-organization and the spacer's properties

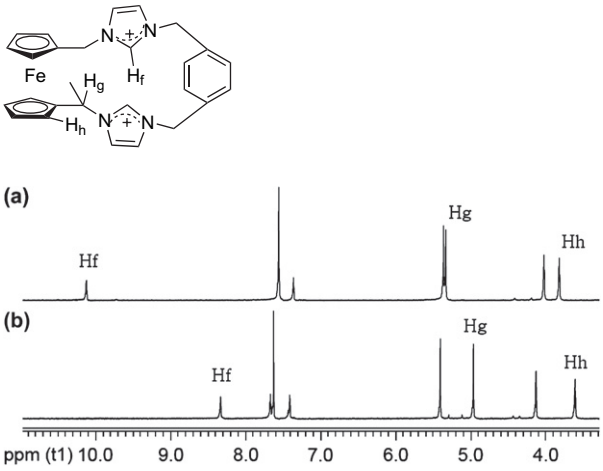

Figure 7. ^{1}H NMR spectra of host **3** before (b) and after (a) the addition of 1 equiv of Cl^- anion in CD_3CN.

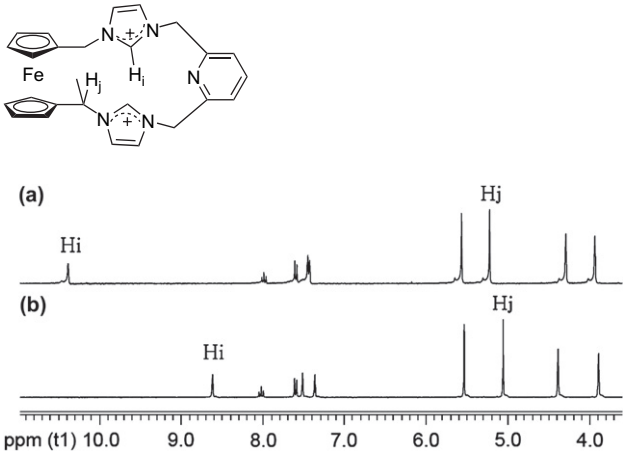

Figure 8. ^{1}H NMR spectra of host **4** before (b) and after (a) the addition of 1 equiv of AcO^- anion in CD_3CN.

of the receptors. Further investigations on imidazolium-based chemsensors are ongoing in our laboratory.

4. Experimental

4.1. General methods

All chemicals and solvents obtained from commercial sources were analytical pure and used without further purification unless emphasized. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-P300 Spectrometer. Chemical shifts δ were reported in parts per million relative to the internal standard TMS for both ^{1}H and ^{13}C NMR. Mass spectra were recorded on a Finnigan LCQ-Advantage spectrometer. Elemental analyses were carried out using a Perkin–Elmer 2400C elemental analyzer.

Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) studies were performed on a BAS-100B electrochemical analyzer in 0.1 M $(n\text{-}Bu)_4NPF_6/CH_3CN$ solution with a glassy carbon electrode as the working electrode at 25 °C (scan rate: 100 mV/s). A 0.01 M $Ag/AgNO_3$ electrode (in 0.1 M $(n\text{-}Bu)_4NPF_6/CH_3CN$) was employed as reference electrode and a Pt electrode (Φ=0.3 mm) was used as the supporting electrode. Redox potentials versus the ferrocenium/ferrocene redox couple were reported. Redox potential shifts were obtained after an excess of anions was added to the solution of the receptors **1**–**4** in CH_3CN (5×10^{-4} M) containing 0.1 M $(n\text{-}Bu)_4NPF_6$.

Table 3
X-ray crystallographic data of complexes **1**·2(PF_6^-), **1**·2(Br^-), **2**·2(PF_6^-), **3**·2(PF_6^-), and **4**·2(PF_6^-)

	1·2(PF_6^-)	**1**·2(Br^-)	**2**·2(PF_6^-)	**3**·2(PF_6^-)	**4**·2(PF_6^-)
CCDC number	673,517	673,519	673,518	673,521	673,520
Empirical formula	$C_{20}H_{24}F_{12}FeN_4P_2$	$C_{20}H_{24}Br_2FeN_4$	$C_{26}H_{26}F_{12}FeN_4P_2$	$C_{26}H_{26}F_{12}FeN_4P_2$	$C_{25}H_{25}F_{12}FeN_5P_2$
Formula weight	666.22	536.10	740.30	740.30	741.29
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*−1	*P* 1 21/*a* 1	*P*2 (1)/*n*	*C* 1 2 1	*P* 1 21/*a* 1
a (Å)	9.795(2)	7.3858(14)	10.9360(15)	13.887(10)	9.0353(9)
b (Å)	11.082(2)	16.673(3)	11.8269(17)	10.322(7)	15.9425(14)
c (Å)	14.063(3)	9.0403(17)	23.256(3)	10.696(8)	19.698(2)
α (°)	70.269(3)	90	90	90	90
β (°)	76.964(4)	106.310(8)	100.088(2)	114.522(5)	103.023(4)
γ (°)	64.909(3)	90	90	90	90
V (A^3)	1295.2(5)	1068.5(3)	2961.4(7)	1394.9(17)	2764.4(5)
Z	2	2	4	4	4
D_{calcd} (g/cm^3)	1.708	1.666	1.660	1.763	1.781
μ (mm^{-1})	0.811	4.458	0.719	0.763	0.771
Total reflections	6736	7824	16,626	5260	24,605
Unique reflections	4552	1849	6021	2392	6167
R_1/wR_2 [$I>2\sigma(I)$]	0.0564/0.1488	0.0613/0.1486	0.0520/0.1323	0.0313/0.0760	0.0678/0.1282
R_1/wR_2 (all data)	0.0785/0.1692	0.0668/0.1525	0.0903/0.1564	0.0324/0.0766	0.0848/0.1366
GoF on F^2	1.057	0.960	1.013	1.025	1.165

4.2. Preparation of cleft-like receptor 1

A solution of PBr_3 (0.38 ml) in benzene (8 ml) was added dropwise to a solution of 1,1′-bis(hydroxymethyl)ferrocene **5** (600 mg) in benzene (60 ml) and THF (20 ml) containing pyridine (0.26 ml) at 0 °C under N_2. The reaction mixture was stirred at room temperature for 4.5 h. Ethanol (3 ml) was added to the mixture and stirring was continued for 0.5 h. The resulting precipitate was removed by filtration and the filtrate was evaporated to dryness. The residue was washed with ethyl acetate/petroleum ether (1:1), filtered, and evaporated under vacuum. The crude yellow solid was used directly in the next step. The solution of 1,1′-bis-(bromomethyl)ferrocene **6** in CH_3CN (25 ml) was added dropwise to the solution of 1-methylimidazole (4 mmol) in CH_3CN. Then, the mixture was refluxed overnight, cooled, and evaporated under vacuum. The residue was dissolved in water (5 ml) and a saturated solution of NH_4PF_6 (2 ml) was added. The resulting yellow solid was filtered to give crude product. Analytical pure product was obtained after crystallization from acetone. Yield 35% (from 1,1′-bis(hydroxymethyl)ferrocene); mp 212–213 °C (dec); ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.81 (s, 6H), 4.29 (s, 4H), 4.47 (s, 4H), 5.15 (s, 4H), 7.65 (s, 2H), 7.70 (s, 2H), 9.02 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 36.50, 48.69, 70.61, 70.66, 82.28, 122.62, 124.41, 136.54; ESI-MS: *m*/*z* 520.96 $(M-PF_6)^+$. Calcd for $C_{20}H_{24}F_{12}FeN_4P_2$: C 36.06, H 3.63, N 8.41. Found: C 36.17, H 3.70, N 8.37.

4.3. General procedure for the preparation of cyclic receptors 2–4

A solution of 1,1′-bis(imidazolylmethyl)ferrocene **7** (225 mg, 0.65 mmol) in CH_3CN (50 ml) and a solution of the dibromides *m*-xylylene dibromide/*p*-xylylene dibromide/2,6-bis(bromomethyl)-pyridine (0.65 mmol) in CH_3CN (50 ml) was added dropwise simultaneously to 250 ml CH_3CN at room temperature. Then, the solution was refluxed overnight under N_2. After cooling to the room temperature, the solvent was evaporated under vacuum. The residue was dissolved in water (5 ml) and a saturated solution of NH_4PF_6 (2 ml) was added. The resulting yellow solid was filtered to give crude product. Analytical pure product was obtained after crystallization from acetone.

Receptor ***2***. Yield 58%; mp 196–198 °C (dec); ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.85 (s, 4H), 4.39 (s, 4H), 5.15 (s, 4H), 5.55 (s, 4H), 6.79 (s, 1H), 7.57–7.62 (m, 3H), 7.74 (s, 2H), 7.90 (s, 2H), 9.36 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 48.56, 52.31, 66.70, 70.65, 85.10, 123.32, 124.76, 125.02, 129.64, 130.28, 137.01, 137.52; ESI-MS: *m*/*z* 645.13 $(M-PF_6)^+$. Calcd for $C_{26}H_{26}F_{12}FeN_4P_2$: C 42.18, H 3.54, N 7.57. Found: C 42.08, H 3.79, N 7.77.

Receptor ***3***. Yield 45%; mp 219–220 °C (dec); ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.49 (s, 4H), 4.13 (s, 4H), 5.00 (s, 4H), 5.44 (s, 4H), 7.64 (s, 4H), 7.77 (s, 2H), 7.98 (s, 2H), 9.12 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 48.51, 53.24, 66.82, 70.09, 85.05, 123.37, 123.82, 130.51, 137.17, 138.13; ESI-MS: *m*/*z* 647.04 $(M-PF_6)^+$. Calcd for $C_{26}H_{26}F_{12}FeN_4P_2$: C 42.18, H 3.54, N 7.57. Found: C 41.90, H 3.79, N 7.66.

Receptor ***4***. Yield 72%; mp 209–210 °C (dec); ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.39 (s, 4H), 4.40 (s, 4H), 5.12 (s, 4H), 5.64 (s, 4H), 7.63–7.66 (m, 4H), 7.84 (s, 2H), 8.06 (t, *J*=7.72 Hz, 1H), 9.26 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 48.35, 53.29, 67.39, 70.33, 85.39, 123.81, 123.88, 124.20, 137.79, 139.35, 154.06; ESI-MS: *m*/*z* 647.04 $(M-PF_6)^+$. Calcd for $C_{25}H_{25}F_{12}FeN_5P_2$: C 40.51, H 3.40, N 9.45. Found: C 40.53, H 3.49, N 9.40.

4.4. ^{1}H NMR titration

In a typical anion titration experiment, aliquots of concentrated solution (0.25 M) of anions in the form of their tetrabutylammonium salts in CD_3CN were added to a 0.5 ml of 5 mM solution of receptors **1**–**4** in CD_3CN.

4.5. X-ray crystallography

The diffraction data were measured on a BRUKER SMART 1000 CCD diffractometer with Mo Kα radiation (λ=0.71073 Å) by ω scan mode at 293(2) K. All data were corrected by semi-empirical method using SADABS program. The program SAINT[14] was used for integration of the diffraction profiles. The structure was solved by the direct methods using SHELXS program of the SHELXL-97 package and refined with SHELXL.[15] The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2. The hydrogen atoms were placed in the geometrically calculated positions. All hydrogen atoms were included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. Crystallographic data and refinement parameters of the five crystals are summarized in Table 3.

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Supplementary data

NMR spectra, partial electrochemical spectra, and crystal structures are available in supplementary data. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.04.098.

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