Anion recognition and sensing of ruthenium(II) and cobalt(II) sulfonamido complexes

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A series of artificial receptors, based on a sulfonamido system, have been designed and synthesized. The interaction of these receptors with biologically important anions was determined by UV-vis, ^{1}H NMR titration and electrochemical experiments. Results indicate that these receptors show high recognition abilities for fluoride (F^-) or acetate (AcO^-), moderate affinities for dihydrogen phosphate ($H_2PO_4^-$) or hydroxyl (OH^-) and almost no affinities for chloride (Cl^-), bromide (Br^-) or iodide (I^-). ^{1}H NMR titration shows that the interaction between the receptors and anions depends on the hydrogen-bond formation. The Co^{III}/Co^{II} redox signals of receptor **3** and **4** disappear gradually when the fluoride or acetate anions are added. Moreover, visual color changes accompany guest binding, enabling this system to act as colorimetric anion sensors. The colorimetric properties of these sensors are ascribed to the hydrogen-bond formation and the colorimetric group quinoxaline.

Introduction

In recent years, increasing attention in the field of host–guest chemistry has been devoted to the fast development of anion recognition systems.[1–9] Considerable attention has focused on the design of anion receptors because of the important roles of the anion in chemical and environmental fields.[10] Artificial anion receptors have presented a lot of special application prospects in the fields of anion sensors,[11–13] phase-transfer catalysts[14] and separation and anion-selective electrodes *etc.*[15,16] Also anions acting as environmental pollutants have only recently been realized and synthetic chemosensors have been developed. It is important for researchers to design chemosensors which show the specific recognition ability for a certain anion and can convert the recognition event into a signal.[17] In particular, it is important to develop colorimetric anion sensing technology by which the naked eye detection can offer qualitative and quantitative information.[18]

Anions are ubiquitous throughout biological systems. They carry genetic information (DNA is a polyanion), and the majority of enzyme substrates and co-factors are anionic. Recently, biological anions such as pyruvate and glutamate have attracted researches' attention.[19,20] Among the range of biologically important anions, the fluoride anion has attracted growing attention due to its established role in preventing dental caries. Fluoride anion is also being explored extensively as a treatment for osteoporosis, a type of fluoride toxicity that generally manifests itself clinically in terms of increasing bone density. Acetate is a critical component of numerous metabolic processes. Acetate production and oxidation rate have been frequently used as an indicator of organic decomposition in marine sediments.[21] Phosphate anions are very important anionic species in living organisms. Naturally occurring phosphate-binding protein (PBP) selectively and strongly bind hydrogen phosphate.

The interaction between artificial sulfonamido receptors and anions is related to the hydrogen-bond. Due to the electron-withdrawing effect of the sulfonyl substituent and ruthenium(II) or cobalt(II) metal, the acidity of NH group can increase and the binding ability between NH and anions is enhanced. In addition cobalt(II) sulfonamido complexes may give an electrochemical response when they interact with anions and can be used as electrochemical sensors. Therefore some reports[22,23] of the receptors, bearing ruthenium metal, for the naked-eye detection of fluoride anion have been published in recent years. And some sulfonamide anion receptors have been synthesized.[24–26] However, the deficiencies of the reported sulfonamide systems are as follows: (1) The binding ability for fluoride anion is not very strong. (2) To the best of our knowledge, there is little research on acetate anion affinity. (3) No colorimetric changes are detectable by the naked eye.

According to this information, we designed and synthesized a series of artificial receptors based on sulfonamido systems (Scheme 1) in order to find a receptor that shows strong binding abilities for fluoride or acetate anion and can be used as a convenient naked-eye detector for anions. Results indicate that this series of sulfonamido receptors shows high sensitivity for F^- or AcO^- among F^-, Cl^-, Br^-, I^-, AcO^-, OH^-, $H_2PO_4^-$, and can thus be used as convenient detectors for F^- or AcO^- due to the visible color changes.

Experimental

Most of the starting materials were obtained commercially and all reagents and solvents used were of analytical grade. All anions, in the form of tetrabutylammonium salts, were purchased from Sigma-Aldrich Chemical Co., stored in a desiccator under vacuum containing self-indicating silica, and used without any further purification. Dimethyl sulfoxide (DMSO) was distilled *in vacuo* after dried with CaH_2. Tetra-n-butylammonium salts (such as

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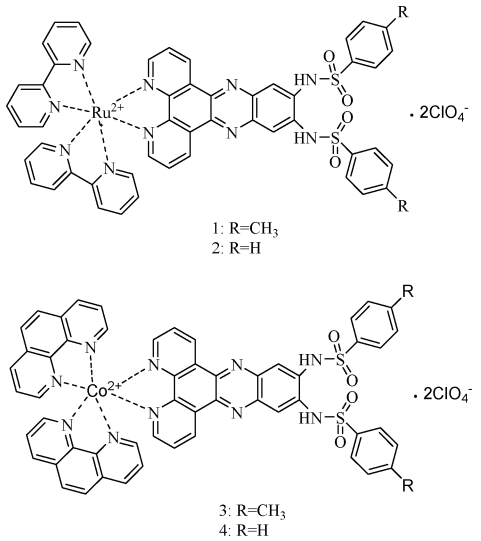


1: R=CH_3
2: R=H

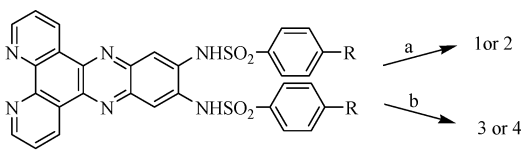
3: R=CH_3
4: R=H

Scheme 1 The structure of receptors.

$(n\text{-}C_4H_9)_4NF$, $(n\text{-}C_4H_9)_4NCl$, $(n\text{-}C_4H_9)_4NBr$, $(n\text{-}C_4H_9)_4NI$, $(n\text{-}C_4H_9)_4NAcO$, $(n\text{-}C_4H_9)_4NOH$, and $(n\text{-}C_4H_9)_4NH_2PO_4$) need to be dried for 24 h in vacuum with P_2O_5 at 333 K before use. C, H, N elemental analyses were made on a Vanio-EL. ^{1}H NMR spectra were recorded on a Varian UNITY Plus-400MHz Spectrometer. Magnetic property was performed on 9600VSM. Electron Paramagnetic Resonance (EPR) spectroscopy was recorded on Bruker EMX-6/1 at 298 K. Electrochemical measurements were performed using a CH-Instruments-430 potentiostat interfaced with Pentium PC. A platinum wire was used as an auxiliary electrode, a Ag/AgCl reference electrode was used and the working electrode was glassy carbon electrode (Φ = 3.8 mm). $NaClO_4$ (0.1 mol l^{-1}) was present as the supporting electrolyte. Scan rate was 100 mV s^{-1}. FAB-MS was made on VG ZAB-HS. ESI-MS was performed with a MARINER apparatus. UV-vis spectroscopy titrations were recorded on a Shimadzu UV-2450 Spectrophotometer at 298 K. The affinity constant is obtained using the method of non-linear least square calculation. In the UV-vis spectral analysis, the concentration of receptors is 2×10^{-5} mol l^{-1} in dry DMSO solution. In ^{1}H NMR titrations, the concentration of receptor **2** is 0.1 mol l^{-1} in DMSO-d_6. In electrochemical experiments, the concentration of receptor **4** is 7×10^{-3} mol l^{-1} in dry DMSO solution.

CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with care. The complexes described in this report have, so far, been found to be safe when used in small quantities.

1, **2**, **3** and **4** were synthesized according to the route shown in Scheme 2.



5: R=CH_3
6: R=H

Scheme 2 Reagents and conditions: (a) $Ru(bpy)_2Cl_2$, DMF, 413 K, (b) $Co(phen)_2Cl_3$, DMF, 413 K.

Briefly, 6′,7′-bis[*p*-tolusulfonamido]-quinoxaline-[2′,3′-d]-1,10-phenanthroline-[5,6] (**5**) was synthesized according to the reported process.[27] The preparation of 6′,7′-bis[*p*-tolusulfonamido]-quinoxaline-[2′,3′-d]-1,10-phenanthroline-[5,6] di-2,2′-bipyridine Ru(II) bis-perchlorate (**1**) was the reaction of $Ru(bpy)_2Cl_2$[28] with **5** in DMF followed by a treatment with $NaClO_4$.[29] 6′,7′-Bis-[*p*-tolusulfonamido]-quinoxaline-[2′,3′-d]-1,10-phenanthroline-[5,6] di-1,10-phenanthroline cobalt(II) bis-perchlorate (**3**) was obtained by the reaction of $Co(phen)_2Cl_3$ and **5** in DMF followed by a treatment with $NaClO_4$. 6′,7′-Bis[phenylsulfonamido]-quinoxaline-[2′,3′-d]-1,10-phenanthroline-[5,6] di-2,2′-bipyridine Ru(II) bis-perchlorate (**2**) and 6′,7′-bis-[phenylsulfonamido]-quinoxaline-[2′,3′-d]-1,10-phenanthroline-[5,6]di-1,10-phenanthroline cobalt(II) bis-perchlorate (**4**) were synthesized according to the above process. Here, $Co(phen)_2Cl_3$ was prepared according to the reported process[30] and was confirmed by the elemental analysis and its magnetic properties. To confirm that the oxidation state of cobalt in receptor **3** is II but not III, cyclic voltammetry, magnetic properties and electron paramagnetic resonance (EPR) experiments were performed.

6′,7′-Bis[*p*-tolusulfonamido]-quinoxaline-[2′,3′-d]-1,10-phenanthroline-[5,6] (**5**) was synthesized according to the reported process. ^{1}H NMR(400 MHz DMSO-d_6) δ = 9.51(d, 2H) 9.18(d, 2H) 7.96(m, 2H) 7.85(s, 2H) 7.78(d, 4H) 7.35(d, 4H) 2.33(s, 6H). Elemental analysis: Calcd. for $C_{32}H_{24}N_6S_2O_4 \cdot 2H_2O$ C, 60.18, H, 4.10 N, 13.16, Found: C, 59.81 H, 4.60 N, 12.85%.

6′,7′-bis-[phenylsulfonamido]-quinoxaline-[2′,3′-d]-1,10-phenanthroline-[5,6] (**6**) was synthesized according to the above procedure by replacement of 1,2-bis(*p*-tolusulfonamido)-benzene with 1,2-bis(phenylsulfonamido)-benzene. ^{1}H NMR(400 MHz DMSO-d_6) δ = 9.53(d, 2H) 9.19(m, 2H) 7.98(m, 2H) 7.90(m, 4H) 7.85(s, 2H) 7.63(s, 2H) 7.58(m, 4H). Elemental analysis: Calcd. for $C_{30}H_{20}N_6S_2O_4 \cdot 2H_2O$ C, 57.32, H, 3.82 N, 13.38, Found: C, 57.05 H, 4.14 N, 13.08%.

6′,7′-Bis[*p*-tolusulfonamido]-quinoxaline-[2′,3′-d]-1,10-phenanthroline-[5,6] di-2,2′-bipyridine Ru(II) bis-perchlorate (**1**): **5** (0.1 mmol) reacted with $Ru(bpy)_2Cl_2$ (0.1 mmol) at 413 K for 3 h in DMF (50 ml). The volume of mixture was condensed to about 20 ml, then $NaClO_4 \cdot H_2O$ (1 g) was added and the mixture was stirred for 2 h at room temperature. Then the mixture was poured into *ca.* 200 ml water and the solid was filtered, washed with water and dried in vacuum. ^{1}H NMR(400 MHz DMSO-d_6) δ = 9.48(d, 2H) 8.86(m, 4H) 8.22(s, 2H) 8.10(d, 4H) 7.91(m, 2H) 7.82(d, 4H) 7.75(m, 8H) 7.59(s, 2H) 7.35(d, 2H) 7.27(d, 4H) 2.29(s, 6H). Elemental analysis: Calcd. for $C_{52}H_{40}N_{10}S_2O_{12}Cl_2Ru$ C, 50.65, H, 3.27 N, 11.36, Found: C, 51.02 H, 3.64 N, 11.38%. FAB-MS (*m*/*z*): 1033.3 $(M - H)^+$.

6′,7′-Bis[phenylsulfonamido]-quinoxaline-[2′,3′-d]-1,10-phenanthroline-[5,6] di-2,2′-bipyridine Ru(II) bis-perchlorate (**2**) was synthesized according to the above procedure by replacement of (**5**) with (**6**). ^{1}H NMR(400 MHz DMSO-d_6) δ = 9.51(d, 2H) 8.85(m, 4H) 8.21(m, 2H) 8.16(d, 4H) 7.95(m, 2H) 7.88(d, 4H) 7.92(m, 4H) 7.71(d, 2H) 7.58(m, 2H) 7.53(m, 8H) 7.34(m, 2H). Elemental analysis: Calcd. for $C_{50}H_{36}N_{10}S_2O_{12}Cl_2Ru \cdot H_2O$ C, 49.10, H, 3.13 N, 11.45, Found: C, 48.67 H, 3.39 N, 11.89%. FAB-MS (*m*/*z*): 1004.8 $(M - H)^+$.

$Co(phen)_2Cl_3 \cdot 4H_2O$: Elemental analysis: Calcd. for $C_{24}H_{16}N_4Cl_3Co \cdot 4H_2O$ C, 48.22, H, 4.05 N, 9.37, Found: C, 47.82 H, 4.41 N, 8.96%. Magnetic properties showed Co(III).

6′,7′-Bis[*p*-tolusulfonamido]-quinoxaline-[2′,3′-d]-1,10-phenanthroline-[5,6] di-1,10-phenanthroline cobalt(II) bis-perchlorate (**3**): **5** (0.1 mmol) reacted with $Co(phen)_2Cl_3$ (0.1 mmol) at 413 K for 3 h in DMF (50 ml). The volume of mixture was condensed to about 20 ml, then was added $NaClO_4 \cdot H_2O$ (1 g) and the mixture was stirred for 2 h at room temperature. Then the mixture was poured into *ca.* 200 ml water and the solid was filtered, washed with water and dried in vacuum. Elemental analysis: Calcd. for $C_{56}H_{40}N_{10}S_2O_{12}Cl_2Co$ C, 54.29, H, 3.25 N, 11.31, Found: C, 53.99 H, 3.68 N, 11.62%. FAB-MS (*m*/*z*): 1039.4 $(M - H)^+$.

6′,7′-Bis[phenylsulfonamido]-quinoxaline-[2′,3′-d]-1,10-phenanthroline-[5,6] di-1,10-phenanthroline cobalt(II) bis-perchlorate (**4**) was prepared according to the above procedure by replacement of (**5**) with (**6**). Elemental analysis: Calcd. for $C_{54}H_{36}N_{10}S_2O_{12}Cl_2Co \cdot H_2O$ C, 52.78, H, 3.12 N, 11.40, Found: C, 52.76 H, 3.26 N, 11.81%. ESI-MS (*m*/*z*): 1009.8 $(M - H)^+$.

Results and discussion

To confirm that the oxidation state of cobalt in receptor **3** is II but not III, cyclic voltammetry (Fig. 1), magnetic properties and electron paramagnetic resonance (EPR, Fig. 2) experiments were performed. From Fig. 1, the reductive peak shows at 0.2 V. However, a reductive peak does not appear when the beginning voltage is 0.2 V. This shows compound **3** exits only as Co(II). According to magnetic data, the magnetic susceptibility μ of cobalt in receptor **3** is about 3.4–4.1 BM and suggests that the oxidation state of cobalt is II. The EPR signal of receptor **3** is very weak indeed (Fig. 2) and does not show the expected hyperfine splittings. However, the broad peak at 3272 G indicates that receptor **3** exists as Co(II). This similar phenomenon exists in **4**. Why does the cobalt in compound **3** (or **4**) exist as Co(II) after the reaction between **5** (or **6**) and $Co^{III}(phen)_2Cl_3$? This needs to be investigated further.

The UV-vis spectral titration method is applied extensively to the systems of coordination reaction that can induce absorption spectral change.[31] The interaction of **1**, **2**, **3** and **4** with biological important anions (F^-, Cl^-, Br^-, I^-, AcO^-, OH^-, $H_2PO_4^-$) was investigated through spectrophotometric titrations in dry DMSO by the addition of a standard solution of the investigated anionic tetrabutyl ammonium salt to the solution of **1**, **2**, **3** and **4**.

As shown in Fig. 3a, the spectrum changes remarkably with the increasing of fluoride concentration. Receptor **1** has certain absorption bands centered at 475 nm and 340 nm. The intensity of absorbance at 340 nm decreases and the intensity of absorbance at 475 nm increases when fluoride anion (in the form of tetrabutyl ammonium salt; always the same hereafter) is added. In addition, two new absorbance peaks at 500 nm and 380 nm develop and the intensity of these absorbance increases. At the same time, the color

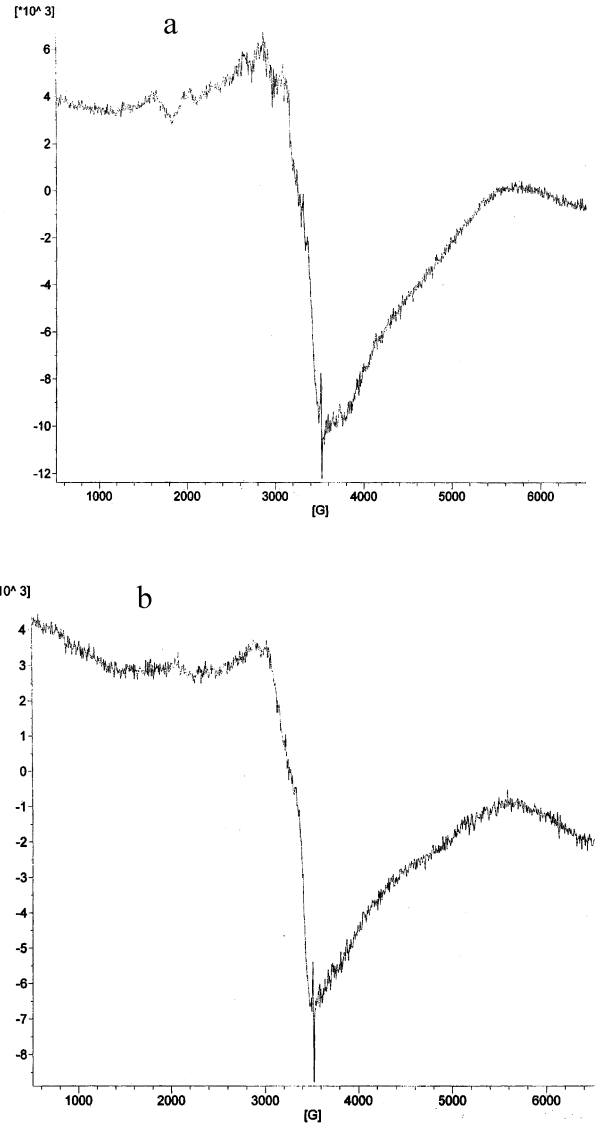


Fig. 2 Electron paramagnetic resonance (EPR) spectroscopy of receptor **3** (a) and **4** (b) at 298 K. Usually, the EPR spectrum signal of these Co(II) compound is indeed weak and does not show expected hyperfine splittings.

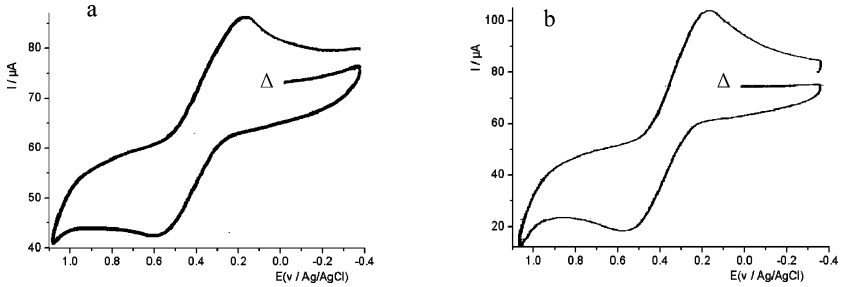


Fig. 1 Cyclic voltammetry of receptor **3** (a, 4×10^{-3} mol l^{-1}) and **4** (b, 1×10^{-2} mol l^{-1}) recorded in DMSO at 298 K, supporting electrolyte: $NaClO_4$ (0.1 mol l^{-1}), working electrode: glassy carbon (Φ = 3.8 mm), reference electrode: Ag/AgCl, auxiliary electrode: Pt, scan rate: 100 mV s^{-1}. Δ represents the beginning point of cyclic voltammetry studies.

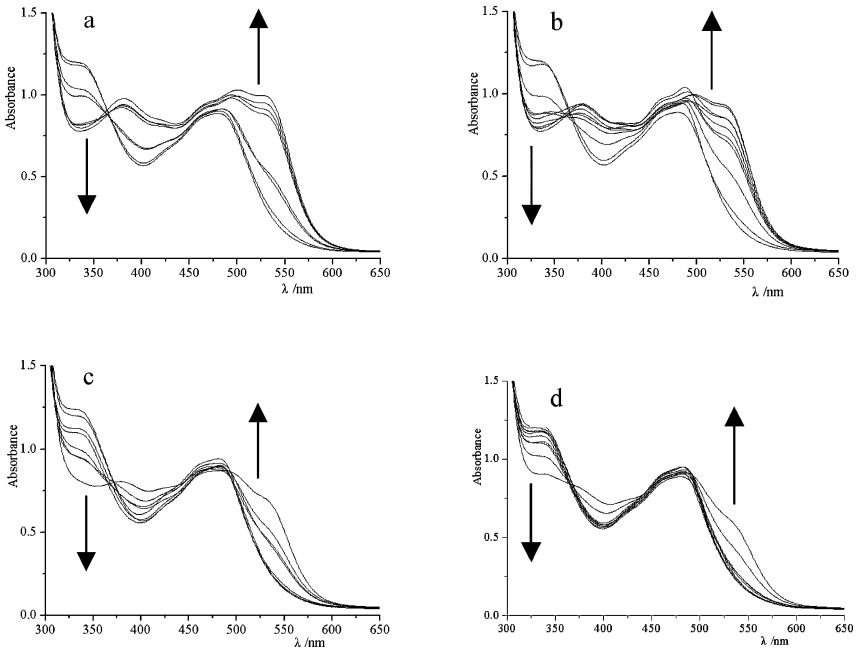


Fig. 3 UV-vis spectral changes of receptor **1** upon the addition of various anions (in the form of tetrabutylammonium salts): (a) F^-, (b) AcO^-, (c) $H_2PO_4^-$, (d) OH^-, [**1**] = 2×10^{-5} mol l^{-1} and [anion] = 0–1.60×10^{-3} mol l^{-1}. Arrows show the increase of anions concentration from 0 to 1.6×10^{-3} mol l^{-1}.

of the solution changes from orange-red to red as fluoride anion concentration increases. After the concentration of fluoride anion reaches 32-fold greater than that of receptor **1**, the changes of intensities of the absorbance and the color of solution are almost stopped. In addition, there appears one clear isosbestic point at 370 nm. This shows that at this point a stable concentration of the complex is formed in the solution with a certain stoichiometric ratio between **1** and F^-. The addition of AcO^- leads to similar spectral changes (Fig. 3b), but the addition of OH^- and $H_2PO_4^-$ shows only small spectral changes (Fig. 3c and Fig. 3d) and the addition of Cl^-, Br^- and I^- leads to virtually no spectral changes.

The spectral changes of receptor **2** interacting with various anions show that the spectral changes of receptor **2** after binding F^- are similar to receptor **1** after binding F^-, as well as AcO^-, $H_2PO_4^-$ and OH^-.

As shown in Fig. 4, the intensity of absorbance at 471 nm increases and there appears two clear isosbestic points at 518 nm and 400 nm with the addition of fluoride anion to **3**, at the same time the color of solution turns deeper gradually. The spectral changes of **4** after binding fluoride anion are similar to that of **3** after binding fluoride anion. The maximum absorption wavelength of **3**–anion complex (or **4**–anion complex) is almost the same as the one of receptor **3** (or **4**). The spectral changes of **3** (or **4**) upon the addition of AcO^-, $H_2PO_4^-$, and OH^- are similar to that of F^-. While, when Cl^-, Br^-, I^- are added the spectral changes almost do not occur.

Affinity constants for the receptors with anionic species are calculated according to the eqn (1) of 1 : 1 host–guest complexation.[32–34]

$$X = X_0 + 0.5\Delta\varepsilon\{c_H + c_G + 1/K_s - [(c_H + c_G + 1/K_s)^2 - 4c_H c_G]^{1/2}\} \quad (1)$$

where, c_G and c_H are the concentration of guest and host, respectively. X is the absorbance intensity at certain concentration of host and guest. X_0 is the absorbance intensity of the host alone. K_s is the affinity constant for the host–guest complexation. $\Delta\varepsilon$ is the change in molar extinction coefficient.

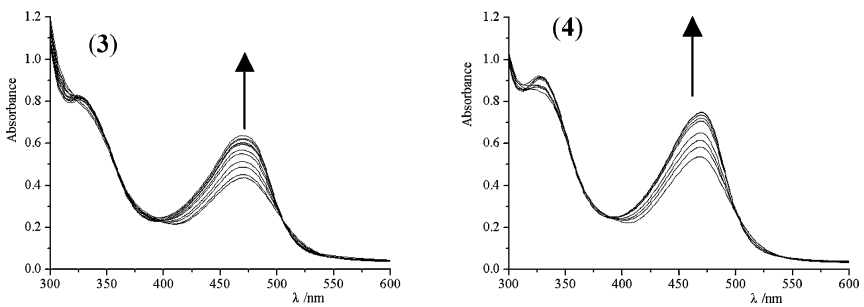


Fig. 4 UV-vis spectral changes of receptor **3** and **4** upon the addition of fluoride anion (in the form of tetrabutylammonium salt): [**3**] = [**4**] = 2×10^{-5} mol l^{-1} and [F^-] = 0–2.0×10^{-4} mol l^{-1}. Arrows show the increase of fluoride anion concentration from 0 to 2.0×10^{-4} mol l^{-1}.

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

Anions	F^-	AcO^-	$H_2PO_4^-$	Cl^-, Br^-, I^-
K_s(**1**)/mol^{-1} L	$(8.90 \pm 1.53) \times 10^3$	$(1.35 \pm 0.32) \times 10^4$	$(5.99 \pm 1.42) \times 10^2$	ND[a]
K_s(**2**)/mol^{-1} L	$(4.47 \pm 0.37) \times 10^4$	$(6.60 \pm 1.06) \times 10^4$	$(3.81 \pm 0.52) \times 10^3$	ND[a]
K_s(**3**)/mol^{-1} L	$(1.39 \pm 0.20) \times 10^5$	$(5.70 \pm 1.20) \times 10^4$	$(5.58 \pm 0.75) \times 10^4$	ND[a]
K_s(**4**)/mol^{-1} L	$(2.42 \pm 0.96) \times 10^5$	$(1.09 \pm 0.11) \times 10^5$	$(8.77 \pm 1.04) \times 10^4$	ND[a]

[a] ND = can not be determined.

Job plot curves indicate the receptors (**1**, **2**, **3** and **4**) bind anions at 1 : 1 ratio. The affinity constants are obtained using the method of non-linear least square calculation. The results are summarized in Table 1 (Cl^-, Br^- and I^- almost have no interactions with receptors and the affinity constants cannot be determined).

Obviously, the anion binding abilities of Ru(II) complexes are in the order of $AcO^- > F^- > H_2PO_4^- \gg OH^- > Cl^-$, Br^-, I^-, and that of Co(II) complexes are in the order of $F^- > AcO^- > H_2PO_4^- > OH^- \gg Cl^-$, Br^-, I^-. The reason may be that the spatial steric hindrance of oxygen atoms of sulfonamido limits the interaction of receptors with anions in space, and only the space-matched anion may have strong binding ability with receptors. For Ru(II) and Co(II) receptors, those different orders may be explained by the change of configuration due to the different coordination details of different metals according to optimized geogmetries of receptors. The geometries of receptors **1–4** were optimized (Fig. 5) using the HF (Hartree–Fock) method with basis sets LANL2DZ for the Fe atom and 3-21G for other atoms. The calculation was performed with Gaussian03 program.[35] From Fig. 5, the distance between two hydrogen atoms in sulfonamide NH (H1–H1′) is 3.178 Å for receptor **1**, 2.428 Å for receptor **2**, 1.630 Å for receptor **3**, 1.669 Å for receptor **4**. The H1–H1′ distance in Ru complexes is larger than that in Co complexes. This shows Ru complexes have highest binding ability for AcO^- and Co complexes for F^- among studied anions. On the other hand, the affinity constants for the same anion with different receptors are $–CH_3 < –H$. The electron-donating ability of the substituents ($–CH_3$) can increase the electron density on the –NH of receptors and decrease its binding ability with anions. Thus, the affinity constants of anion complexes decrease with the increase of electron-donating ability.

The previously reported sulfonamido system[24] has strong affinity to chloride anion because the coordination space formed between two –NH groups, which are located in *meta*-configuration, is better fit for the size of chloride anion. The two –NH of our sulfonamido system are in *ortho*-configuration. According to the optimized geogmetry the space for anionic coordination of our system is better fit for the size of fluoride and acetate anion. Therefore, sulfonamido receptors with –NH located in *ortho* positions have a strong affinity to fluoride and acetate anion, and Crabtree's sulfonamido with –NH located in *meta* positions may have strong selectivity for chloride anion. The advantages of using receptors **1–4** for the detection of various anions are as follows: (1) the receptors have strong binding ability for F^- and AcO^-; (2) The receptors accompany visible color changes when they interact with F^- and AcO^-. Therefore, the sulfonamido complexes may be used as convenient naked-eye detection tool, such as the detection of F^- in toothpaste.

The binding ability of receptor **1** and **2** with acetate anion is the strongest, while the binding ability of receptor **3** and **4** with fluoride anion is the strongest among the studied anions according to affinity constant. The above results derive from the condition that only one anion exists. To test if the binding ability of acetate or fluoride changes when all studied anions are present simultaneously, we conducted a UV-vis spectral experiment. Fig. 6 shows that the spectral response of **2** upon the addition of acetate is almost the same as the that with addition of AcO^- and other anions. It indicates that the binding ability of acetate with receptor **2** is not influenced by the existence of other anions. Similarly, the binding ability of acetate with receptor **1** is not influenced by the existence of other anions. This point has experimental and practical importance.

Very recently, a number of fluorogenic and/or chromogenic anion sensors comprising recognition moieties with acidic protons such as urea, thiourea, or amide have been reported to undergo an anion-induced deprotonation.[36–38] According to these reports, there appears one new triplet resonance at 16.1 ppm, the characteristic resonance of bifluoride (F–H–F^-). In addition, the chemical shifts of the non-interacted sites occur remarkable changes. To look into the anion binding properties of receptor **2** for F^- and AcO^-, ^{1}H NMR titration experiments in DMSO-d_6 are performed (Fig. 7). However, a new triplet resonance at about 16.1 ppm does not appear in this system when fluoride anion is added (Fig. 7) (we did ^{1}H NMR titration from 0 to 20 ppm but no new triplet peak appeared at about 16.1 ppm therefore the data is only shown to 9.7 ppm), at the same time, phenyl proton signals (9.4–7.3 ppm) do not exhibit significant changes in chemical shifts. Such phenomena are also perceived, upon the addition of acetate anion, in the ^{1}H NMR spectrum. The above results indicate that receptor **2** does form hydrogen bonds between the sulfonamide protons and fluoride or acetate anion. The electron cloud density of amide in receptor **1** is stronger than that in receptor **2** due to the electron-donating effect of $–CH_3$. Therefore, the interaction of receptor **1** with anions is weaker than that of receptor **2**, and receptor **1** may not occur deprotonation when it interacts with fluoride or acetate anion. This suggests that hydrogen bonds are formed between –NH and anion.[39]

The electrochemical detection of anionic species is particular challenge. To further explore **3** and **4** as electrochemical anion sensors, cyclic voltammetry (CV) studies were performed in DMSO. Fig. 8a is the cyclic voltammetry of AcO^- and it can be concluded that no cyclic voltammetry signal exists for AcO^-. Fig. 8b illustrates the effect of acetate binding on the cyclic voltammetry of **4**. The Co^{III}/Co^{II} redox response weakens to disappear gradually on addition of AcO^-, and the Co^{III}/Co^{II} redox peak potential moves gradually to a more positive potential. These changes are interpreted in terms of the complex formation between **4** and AcO^-. The similar phenomenon exists upon the addition of F^-, compared with AcO^-. However, the addition of $H_2PO_4^-$ or

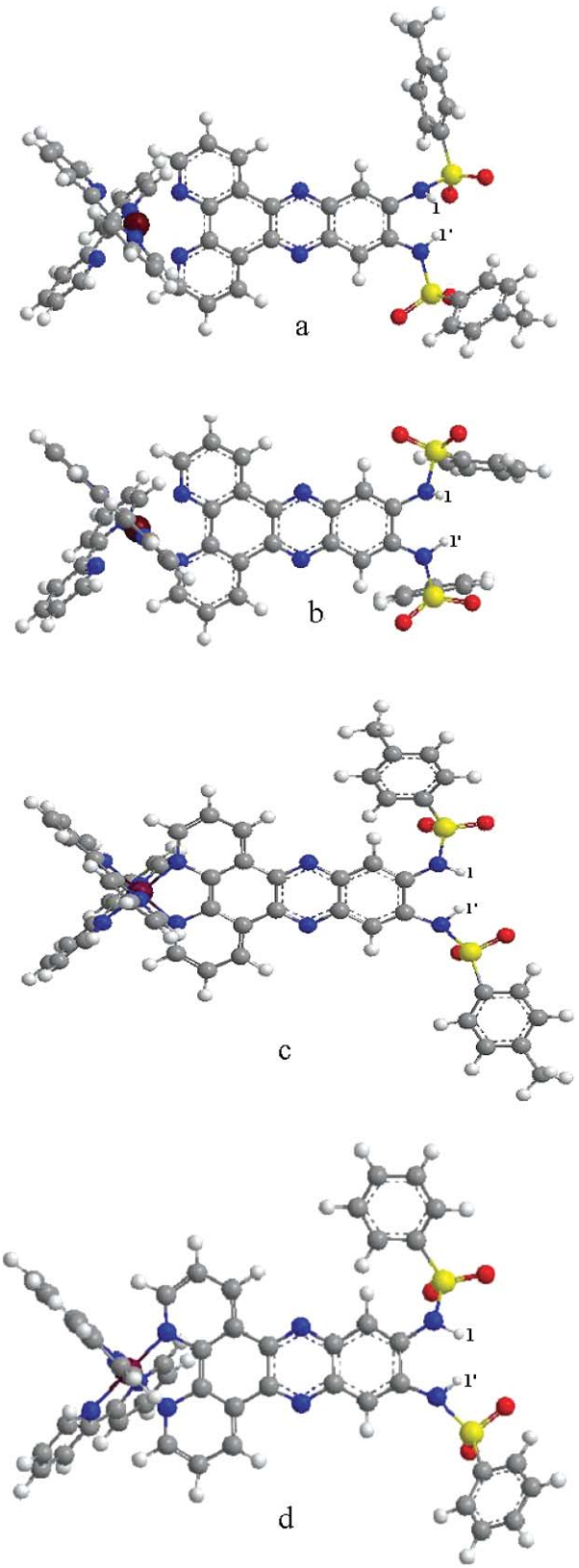


Fig. 5 Optimized configuration of receptor **1** (a); **2** (b); **3** (c); **4** (d).

OH^- leads merely to the decrease of Co^{III}/Co^{II} redox signal. This shows that the binding abilities of $H_2PO_4^-$ and OH^- with receptors are weaker than that of F^- and AcO^-. The additions of Cl^-, Br^- and I^- lead to almost no change of the intensity of the Co^{III}/Co^{II} redox signal. This suggests that there are almost no electrochemical response between Cl^-, Br^-, or I^- and the receptors.

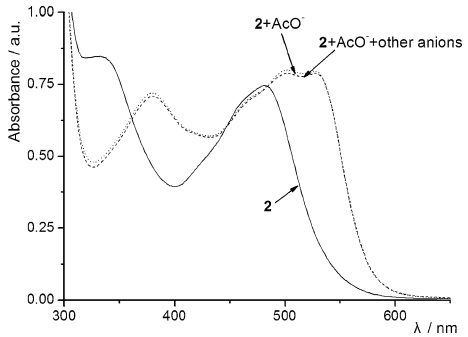


Fig. 6 UV-vis spectral changes of receptor **2** upon the addition of anions [**2**] = 2×10^{-5} mol l^{-1}, the concentration of anions is 10 equiv. **2**.

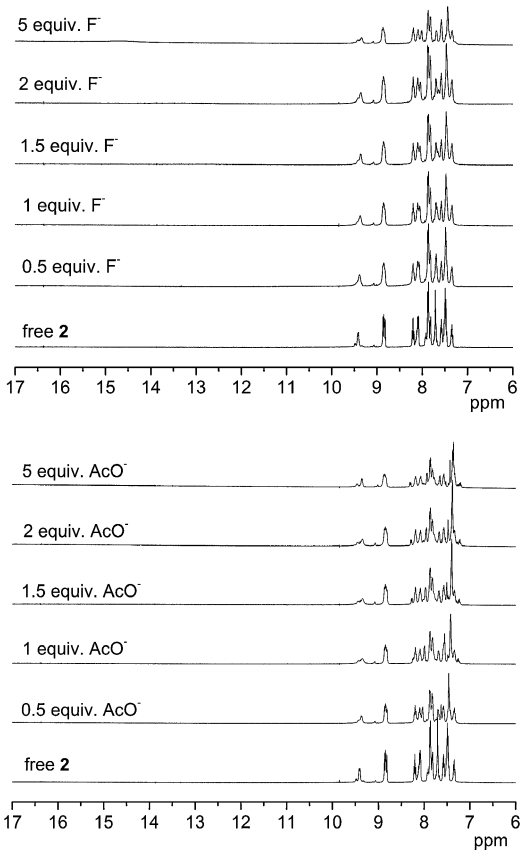


Fig. 7 Plots of ^1H NMR spectra of receptor **2** (0.1 mol l^{-1}) in DMSO-d_6 upon the addition of various quantities of Bu_4NF and Bu_4NAcO (from 0 to 5 equiv.).

Conclusions

In summary, we have studied the recognition properties of **1**, **2**, **3** and **4** with the biological important anions (F^-, Cl^-, Br^-, I^-, AcO^-, OH^- or $H_2PO_4^-$) by UV-vis, ^1H NMR titration and electrochemical experiments. Results indicate that **1**, **2**, **3** and **4** show strong affinities for F^- or AcO^-, moderate affinities for $H_2PO_4^-$ or OH^- and almost no affinities for Cl^-, Br^- or I^-. What's more, the interaction of the artificial receptors with F^-

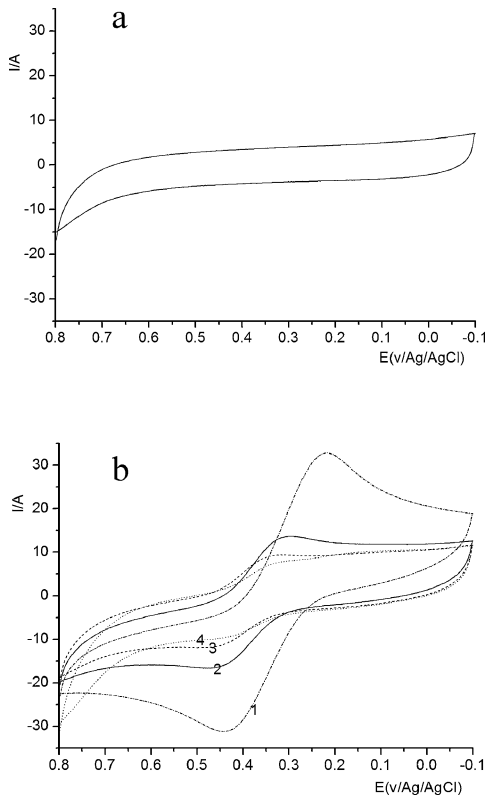


Fig. 8 Cyclic voltammetry of AcO^- (a, 7×10^{-3} mol l^{-1}) and receptor **4** (b, 7×10^{-3} mol l^{-1}) recorded in DMSO at 298 K, (1) free receptor **4**; (2) receptor **4** + 0.1 equiv. AcO^-; (3) receptor **4** + 0.5 equiv. AcO^-; (4) receptor **4** + 1 equiv. AcO^-, supporting electrolyte: $NaClO_4$ (0.1 mol l^{-1}), working electrode: glassy carbon (Φ = 3.8 mm), reference electrode: Ag/AgCl, auxiliary electrode: Pt, scan rate: 100 mV s^{-1}.

and AcO^- causes visible color changes which make the receptors colorimetric sensors. The colorimetric properties of these sensors are ascribed to the hydrogen-bond formation and the colorimetric group quinoxaline. By changing the substitution site on the phenyl ring, for example, from *para* to *ortho*, the selectivity between fluoride and acetate may be finely tuned. The correlations between the electronic properties of the substituent and the affinity, as well as the selectivity and the configuration of receptor, will be a very useful guide to design more selective chemosensors to recognize F^- or AcO^-.

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