



Spectral response to oxy-anions based on ferrocenylphalene

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ARTICLE INFO

Article history:

Received 9 September 2011

Received in revised form 18 January 2012

Accepted 22 January 2012

Available online 8 February 2012

Keywords:

Chemosensor

Ferrocene

Phenol group

Theoretical investigation

ABSTRACT

A series of ferrocenyl derivatives (**1**, **2**, **3** and **4**) containing phenol group, chemosensors for anions, have been synthesized and optimized. Their binding ability for various anions (F^- , Cl^- , Br^- , I^- , AcO^- and $H_2PO_4^-$) were evaluated by theoretical investigation, UV–Vis, 1H NMR titration and cyclic voltammetry experiments and these chemosensors showed strong binding ability for oxy-anions. Theoretical investigation analysis revealed the substituent was different, the space structure was different. And the intramolecular hydrogen bond existed between $-OH$ and other atoms in the structure of these compounds. UV–Vis titrations indicated the anion binding abilities could be tuned by electron push–pull properties of the substituents on the phenyl ortho or para position. Electrochemical titrations showed the addition of anions led to the weak of redox response and the oxidation peak potential moved to more positive potential gradually. In addition, these chemosensors were sensitive to the AcO^- detection without the interference of other anions studied, as well as chemosensor **4** was sensitive to the $H_2PO_4^-$ detection.

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1. Introduction

Artificial anion receptors have attracted increasing attention in the field of host–guest chemistry due to their medicinal and environmental potential [1–10]. The structural design of these receptors has been focused on having the ability to selectively recognize and sense the biologically important anions [11–13]. Anions, ubiquitous throughout biological systems, carry genetic information (DNA is a polyanion), and the majority of enzyme substrates and co-factors are anionic [5]. Anions also play roles in the areas of medicine and catalysis such as pollutant anions that have been linked to eutrophication of rivers and carcinogenesis. While a number of synthetic receptors for anions have been designed, it is often difficult to control selectivity and binding ability because of their wide range of geometries, low ratios of charge to radii among spherical, “Y” shape and tetrahedral shape anions, etc. The excellent stability of ferrocene and its derivatives coupled with their favorable electrochemical properties make these derivatives suitable as receptors for sensor devices with electrochemical detection [14–17]. The ferrocene-based receptors can interact with anions via electrostatic interaction, hydrogen bonding, hydrophobic interaction, or a combination of two or more of these interactions. Furthermore, ferrocene-based receptors with molecular clefts or cavities can

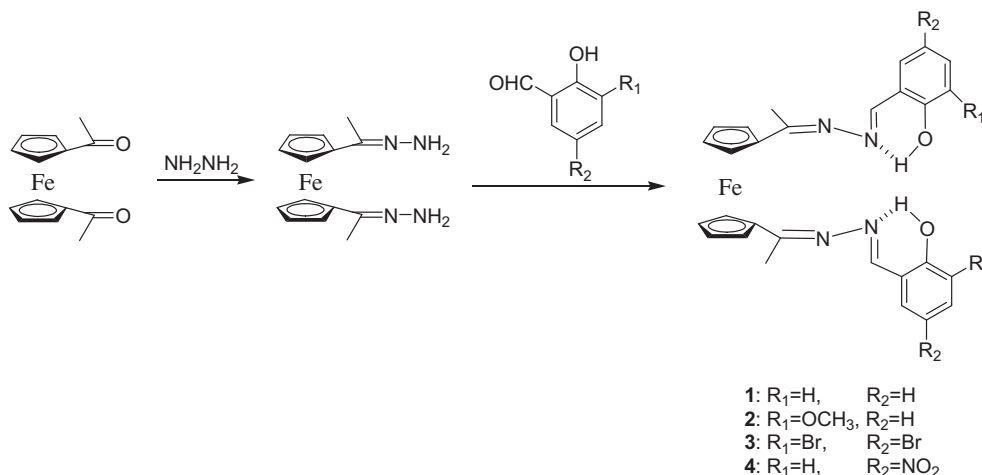
discern anions with different geometries or hydrogen bonding requirements [18–20]. According to the advantage of ferrocene derivatives and hydroxyl group, we designed and synthesized a series of chemosensors based on different substituents (Scheme 1) by tuning the acidity and the hydrogen-bond donor property of the OH moiety with *o*- OCH_3 electron-donating derivative **2**, *o,p*-Br and *p*- NO_2 electron-withdrawing derivative **3** and **4**, respectively. These chemosensors are composed of an electroactive core and two parallel strands of benzene that can interact with different anions by hydrogen bonding with phenol groups. The host–guest complexation for binding different anions (F^- , Cl^- , Br^- , I^- , AcO^- and $H_2PO_4^-$) through UV–Vis, 1H NMR and cyclic voltammetry measurements were investigated.

2. 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 vacuum after dried with CaH_2 . Tetra-*n*-butylammonium salts [such as (*n*- C_4H_9) $_4$ NF, (*n*- C_4H_9) $_4$ NCl, (*n*- C_4H_9) $_4$ NBr, (*n*- C_4H_9) $_4$ NI, (*n*- C_4H_9) $_4$ NAcO and (*n*- C_4H_9) $_4$ NH $_2$ PO $_4$] were dried for 24 h in vacuum with P_2O_5 at 333 K. C, H, N elemental analyses were made on Vanio-EL.

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Scheme 1. Synthesis route of chemosensor **1**, **2**, **3** and **4**.

¹H NMR spectra were recorded on a Varian UNITY Plus-400 MHz Spectrometer. ESI-MS was performed with a MARINER apparatus. UV-Vis Spectroscopy titrations were carried out on a Shimadzu UV2550 Spectrophotometer at 298.0 ± 0.1 K. Electrochemical measurements were performed using a CH-Instruments-430 potentiostat interfaced with Pentium PC. A platinum wire was used as an auxiliary electrode, an Ag/AgCl reference electrode was used and the working electrode was glassy carbon electrode ($\Phi = 3.8$ mm). NaClO₄ (0.1 mol L⁻¹) was present as the supporting electrolyte. Scan rate was 0.1 V s⁻¹.

The compounds were synthesized according to the route shown in Scheme 1.

2.1. 1,1'-Diacetylferrocene

It was synthesized according to reported literature [21].

2.2. 1,1'-Diacetylferrocenedihydrazone

It was synthesized base on (according to) reported literature [22]. Yield: 76%. m.p. 150–152 °C. Elemental Anal. Calc. for C₁₄H₁₈FeN₄: C, 56.39; H, 6.08; N, 18.79. Found: C, 56.21; H, 6.04; N, 18.72%.

2.3. Di(5-(2'-hydroxyl-phenyl)-2,4-dien-3,4-diazapentanyl-2)-ferrocene (**1**)

It was prepared by refluxing 1,1'-Diacetylferrocenedihydrazone (300 mg, 1 mmol) and 2-hydroxyl-benzenealdehyde (244 mg, 2 mmol) in dry ethanol (40 ml) for 12 h. The solid was filtered off and dried in vacuum. Yield: 92%. ¹H NMR (400 MHz, DMSO-*d*₆, 298 K) δ 11.60 (s, 2H), 8.81 (s, 2H), 7.28 (d, 2H), 7.15 (d, 2H), 6.92 (d, 4H), 4.91 (s, 4H), 4.54 (s, 4H), 2.36 (s, 6H). Elemental Anal. Calc. for C₂₈H₂₆FeN₄O₂·H₂O: C, 64.16; H, 5.38; N, 10.69. Found: C, 64.17; H, 5.64; N, 11.05%. ESI-MS (*m/z*): 505.0(M-H)⁻.

The following compounds, (**2**), (**3**) and (**4**) were prepared by similar procedure mentioned above.

2.4. Di(5-(2'-hydroxyl-3'-methoxyphenyl)-2,4-dien-3,4-diazapentanyl-2)-ferrocene (**2**)

¹H NMR (400 MHz, DMSO-*d*₆, 298 K) δ 11.41 (s, 2H), 8.44 (s, 2H), 7.85 (d, 4H), 7.78 (d, 2H), 4.82 (s, 4H), 4.51 (s, 4H), 3.89 (s, 6H), 2.34 (s, 6H) Elemental Anal. Calc. for C₃₀H₃₀FeN₄O₄: C, 63.61; H, 5.34;

N, 9.89. Found: C, 63.69; H, 5.59; N, 9.91%. ESI-MS (*m/z*): 565.1(M-H)⁻.

2.5. Di(5-(2'-hydroxyl-3',5'-dibromine-phenyl)-2,4-dien-3,4-diazapentanyl-2)-ferrocene (**3**)

¹H NMR (400 MHz, DMSO-*d*₆, 298 K) δ 12.42 (s, 2H), 8.62 (s, 2H), 7.81 (s, 2H), 7.48 (s, 2H), 5.10 (s, 4H), 4.65 (s, 4H), 2.38 (s, 6H) Elemental Anal. Calc. for C₂₈H₂₂FeBr₄N₄O₂: C, 40.91; H, 2.70; N, 6.82. Found: C, 40.89; H, 3.03; N, 6.86%. ESI-MS (*m/z*): 816.8(M-H)⁻.

2.6. Di(5-(2'-hydroxyl-5'-nitro-phenyl)-2,4-dien-3,4-diazapentanyl-2)-ferrocene (**4**)

¹H NMR (400 MHz, DMSO-*d*₆, 298 K) δ 12.50 (s, 2H), 8.84 (s, 2H), 8.15 (d, 2H), 6.78 (d, 2H), 5.11 (s, 4H), 4.66 (s, 4H), 2.40 (s, 6H) Elemental Anal. Calc. for C₂₈H₂₄FeN₆O₆: C, 56.39; H, 4.06; N, 14.09. Found: C, 56.58; H, 4.21; N, 14.28%. ESI-MS (*m/z*): 595.2(M-H)⁻.

3. Results and discussion

3.1. Characterization of the compounds

In ¹H NMR spectra, the peaks, at 11.60, 11.41, 12.42, and 12.50 ppm can be assigned to the proton of -OH group for compound **1**, **2**, **3** and **4**, respectively. The chemical shift of phenol group reveals their acidic feature, the substituent group will affect on their acidity of the phenol. The stronger electron-withdrawing will lead to more acidic. According to substituent effect, the substituent, -H, OCH₃, Br, NO₂ in compounds **1–4** will expect with order of **4** > **3** > **1** > **2** in acidity, which is consistent with the result of ¹H NMR. In addition, the chemical shift of phenol group can also reflect the anion binding ability, down field shift indicating strong binding ability. The above results can be supported by the other spectral changes.

3.2. UV-Vis spectral analysis

The interaction of the chemosensors with a variety of anions was investigated through UV-Vis spectral titrations in dry DMSO by the addition of a standard tetrabutyl ammonium (TBA) anion salt solution to the chemosensor solution. Fig. 1 showed the UV-Vis spectral changes of four chemosensors during the titration with acetate ion. It is interesting that the color change (from yellow to orange-red) can be seen in chemosensor **1** during the addition of acetate ion, accordingly the peak at about 400 nm decreased and

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