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# Convenient synthesis of new water-soluble monosubstituted functional ferrocene derivatives

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## Abstract

Two new water-soluble monosubstituted functional ferrocene derivatives, *p*-ferrocenyl benzene sulfonic acid (BSAFc) and 4-ferrocenyl-1,1′-azobenzene-3,4′-disulfonic acid (AYFc), bearing sulfonic groups and/or azo structure have been successfully synthesized in aqueous media according to the self-designed synthetic route. The preparation process is quite simple and convenient. $^1$H NMR, FT-IR and element analysis data demonstrated the structures of the target products. UV–Vis spectra and cyclic voltammetry (CV) measurements explained the electrophilic group that linked to BSAFc and AYFc was an influence on the orbital energy level of ferrocene. The CVs in different concentration and type of anion existing in the solution demonstrated that the electrochemical activities of BSAFc and AYFc firmly rely on the anion.

*Keywords:* Ferrocene derivatives; Azo structure; Sulfonic group; Electron-transfer ability

Ferrocene derivatives have long been the focus of research due to their redox center, the π-conjugated system and the resulting exclusive electron-transfer ability. There is considerable interest in the synthesis of new polymers via introducing functional ferrocene derivative structure because of their potential applications in optical, electronic and magnetic materials [1]. However, the reports relating to conductive polymers with ferrocene moiety are scarce.

As far as know, most of the known ferrocenyl compounds are only soluble in hydrophobic media that limited their application in aqueous systems [2,3]. Knox et al. [4] had reported the preparation of water-soluble Ferrocenyl sulfonic acid (SAFc) by sulphonation of ferrocene at the presence of reagent of chlorosulphonic acid in acetic anhydride. The synthetic method was complex and not environment friendly. In this paper, we designed and synthesized two new water-soluble ferrocene derivatives with sulfonic groups and/or azo structure, which possess the excellent solubility in water and could be worked into conductive polymer as a dopant. These compounds were characterized by $^1$H NMR, FT-IR, UV–Vis spectrum, elemental analyses, atomic absorption spectrum, cyclic voltammetry and melting point measurement. $^1$H NMR was recorded on a Bruker DPX 300 instrument operating at a proton frequency of 300 MHz; elemental analyses were performed on a Heraeus CHN–O–Rapid instrument; atomic absorption spectra were obtained on a Hitachi 180-80 instrument; UV–Vis spectra were carried out on UV-3100 PC Shimadzu in the range of 200–800 nm; FT-IR spectra were recorded on a Bruker IFS 66V instrument in the range of 400–4000 cm$^{-1}$; Melting points were determined on an X-4 digital display micro melting point apparatus. The CV curves were performed in a one-compartment three-electrode

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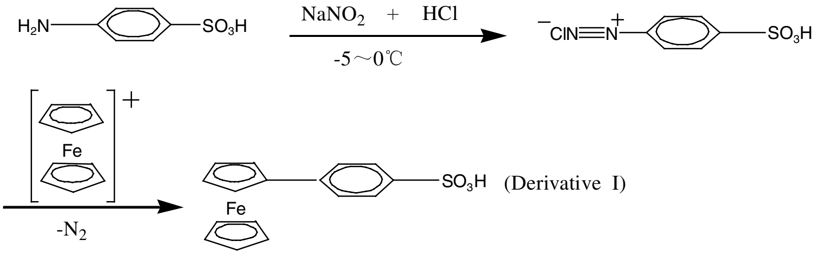
cell with the use of a PARC M273 potentiostat under the nitrogen atmosphere monitored by a computer at room temperature.

The compounds, *p*-ferrocenyl benzene sulfonic acid (BSAFc, **I**) and 4-ferrocenyl–1,1′-azobenzene-3,4′-disulfonic acid (AYFc, **II**), were prepared according to the procedures we designed as shown in Schemes 1 and 2.

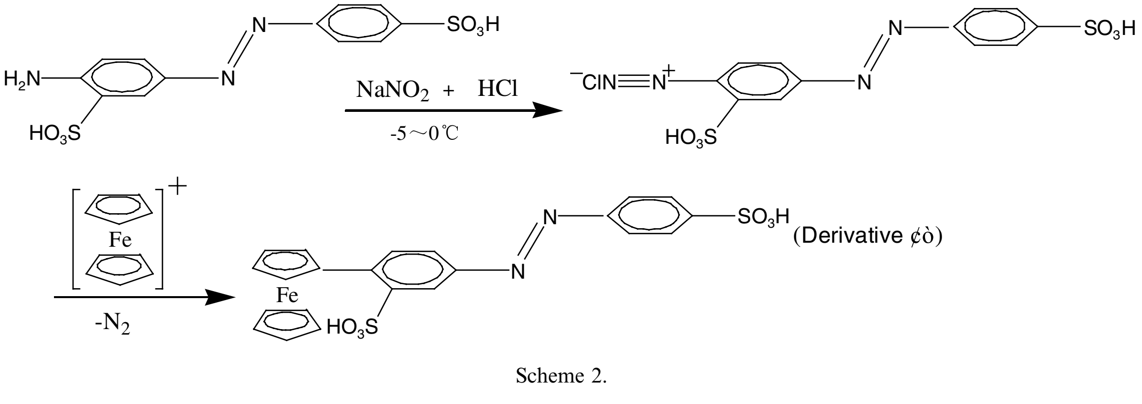
It is well known that the derivatives of ferrocene have been made usually from ferrocene in its organic solvent soluble form. Nevertheless, cationic form $[Fe(C_5H_5)_2]^+$ of ferrocene is also capable of reacting with aromatic diazonium salts in dilute acid medium. $[Fe(C_5H_5)_2]^+$ can be produced by oxidation [5,6] of concentrated sulfuric acid and ferrocene, and employed to react with diazonium salts of aromatic amines in dilute sulfuric acid medium at room temperature. Reactions occur with nitrogen evolution and ferrocene derivatives substituted with one or more aryl groups are obtained. The monoaryl ferrocene derivatives are usually formed at lower yield and are always present in the cationic, dilute-acid soluble form, which can be precipitated readily by adding a reducing agent such as ascorbic acid. However, the quantity of reducing agents is rather difficult to be determined. In this paper, we chose to add solid NaOH into the dilute acid solution and adjusted the pH value of the system. Precipitates containing the target products appear immediately as soon as the solution becomes neutral. As indicated above, this dealing method is simple and convenient.

The synthesis of BSAFc was detailed as follows. Ferrocene (4.6 g, 0.025 mol) was added to 98% sulfuric acid (13 ml, 0.225 mol), while allowing the temperature to rise to 50 °C. Sulfur dioxide was evolved and the dark blue solution of $[Fe(C_5H_5)_2]^+$ resulted. This solution was kept at room temperature overnight, and then poured into ice and water. About 4.33 g of *p*-amino benzene sulfonic acid was diazotized in 36.5% hydrochloric acid (7 ml) at −5 to 0 °C. The newly formed diazonium salt was slowly added to the above solution of $[Fe(C_5H_5)_2]^+$ at 0 °C for 3 h under magnetic stirring. Then, the stirred solution was kept overnight at room temperature. A deep blue acid solution was obtained upon filtration of the above solution. Subsequently, a mixture precipitate containing unreacted ferrocene and *p*-ferrocenyl benzene sulfonic acid resulted instantly when the solution was adjusted to neutral by sodium hydroxide. After removing the unreacted ferrocene by washing the precipitate with acetone and filtrating, the residue was recrystallized from water. Column chromatography (trichloromethane/methanol = 5:1) on silica gel gave *p*-ferrocenyl benzene sulfonic acid (0.8 g, 10% yield) as an orange crystal melting at 246 °C (decomposed) $^1H$ NMR(DMSO): $\delta$ 7.53–7.47(m, 4H), 4.02(s, 5H), 4.35(m, 2H), 4.80(m, 2H). Anal. Calcd. for $C_{16}H_{14}SO_3Fe$: C, 56.14%; H, 4.09%; Fe, 16.37%. Found: C, 56.06%; H, 4.07%, Fe, 15.68%. IR (KBr, $cm^{-1}$): $\nu_{OH}$ 3440(s), $\nu_{C-H}$ 3103 (w), $\nu_{C=C}$ 1650, 1599(m), $\nu_{S=O}$ 1201 (s), 1133 (s).

Compound AYFc was prepared according to a similar procedure used for compound BSAFc via replacing *p*-amino benzene sulfonic acid by Acid yellow 9#. Column chromatography of the concentrated filtrate (trichloromethane/methanol = 3:1) on silica gel produced AYFc (1.4 g, 20% yield) as a black-purple crystal not



Scheme 1.



Scheme 2.

melting below 320 °C. $^1$H NMR(DMSO): $\delta$ 7.88–7.79(m, 7H), 8.07(d, 1H), 8.38(d, 1H), 5.21(m, 2H), 4.30(m, 2H), 4.08(s, 5H). Anal. Calcd. for $C_{22}H_{118}N_2(SO_3)_2Fe$: C, 50.19%; H, 3.42%; N, 5.32%; Fe, 10.65%. Found: C, 51.20%; H, 3.80%; N, 5.31%; Fe, 10.66%. IR (cm$^{-1}$): $\nu_{OH}$ 3426(s), $\nu_{C\text{–}H}$ 3094 (w), $\nu_{C=C}$ 1635(m), 1594(m,) 1395 (w), $\nu_{S=O}$ 1194 (s), 1123 (s).

The UV–Vis spectra of compounds **I** and **II** were displayed in Fig. 1, while the corresponding absorption bands were recorded in Table 1, respectively. The absorption band of compound **I** at 285 nm is attributed to π–π* transition of substituted benzene ring which is red-shifted more than 30 nm compared to that of unsubstituted benzene ring at 254 nm [7]. The shifting of the absorption band to long wavelength is due to that the electrophobic ferrocene group and the electrophilic sulfonic group connected to benzene can respectively increase HOMO level and decrease of LOMO level, which make the energy-level width of substituted benzene narrower. The bands at 247, 341 and 449 nm of compound **I** and 526 nm of compound **II** belong to the d–d transition of monosubstituted ferrocene, which are also red-shifted relative to that of unsubstituted ferrocene at 240 nm, 320 and 435 nm [7] because of the existence of electrophilic sulfonic group. Owing to the longer conjugated chain and better electro-transfer ability of compound **II**, the 91-nm displacement at 526 nm of compound **II** is much greater than that 14-nm displacement at 449 nm of compound **I** compared to the band at 435 nm of unsubstituted ferrocene. The strong band at 348 nm in Fig. 1(b) is belonging to azo group [7] that shows an overlap with the absorption band of substituted ferrocene in compound **II**.

Table 1
UV–Vis spectroscopic parameters for compounds **I**, **II** in aqueous solution at 20 °C

| Compound | $\lambda_{max}$ (nm) | Absorbency $A$ |
|---|---|---|
| **I** | 247.0 | 1.443 |
| | 285.0 | 1.357 |
| | 341.0 | 0.195 |
| | 449.0 | 0.066 |
| **II** | 348.0 | 1.983 |
| | 526.0 | 0.253 |

The electrochemical behaviors of compounds **I** and **II** were investigated in the potential range of 0.0–0.5 V by cyclic voltammetry (CV) which is sensitive electrochemical method and permit the collection of excellent data at low concentration of electro-active substance [8]. The CV curves in Fig. 2 show that the redox characteristics are similar for both compounds. The oxidation peaks of BSAFc and AYFc are all 296 mV and the reduction peaks are 202 and 196 mV, respectively. That is to say, the separation of oxidation and reduction potentials, $\Delta E_P$, are 94 and 100 mV at 100 mV/s, respectively, for BSAFc and AYFc. These values are larger than that expected for reversible one-electron transfer reaction, which is given by 57/$z$ mV, where $z$ is the number of electron transferred in the process [9], indicating that the irreversibility of the electron-transfer process was maintained under this condition. The half-wave potentials of BSAFc and AYFc are 249 and 245 mV which could be figured out easily. Generally, the half-wave potential of monosubstituted ferrocene that linked with electrophilic group would shift towards positive potential compared to unsubtituted ferrocene. Antonietta Baldo et al. [10] had found that the half-wave potential of ferrocene is 190 mV (vs. Ag/AgCl) in pure aqueous solution. There were about 60 mV towards more positive potential of BSAFc and AYFc, which is consistent with the result of UV–Vis spectra.

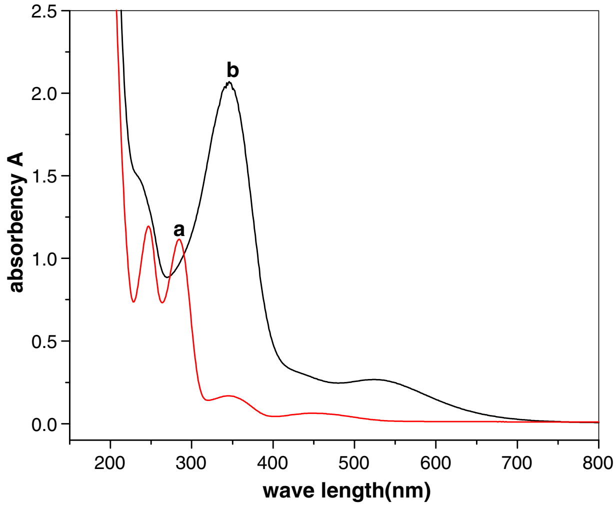


Fig. 1. UV–Vis spectra: (a) BSAFc (**I**) ($1 \times 10^{-4}$M); (b) AYFc (**II**) ($1 \times 10^{-4}$M).

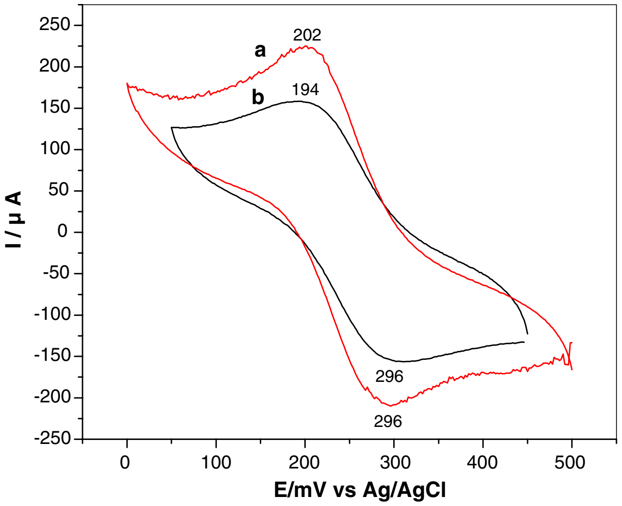


Fig. 2. Cyclic voltammogram of: (a) BSAFc ($1 \times 10^{-3}$ M); (b) AYFc ($1 \times 10^{-3}$ M). Working electrode and auxiliary electrode: Pt disk. Reference electrode: Ag/AgCl (1 M KCl). Scan rate: 100 mV/s. Supporting electrode: NaCl aqueous solution (0.05 M).

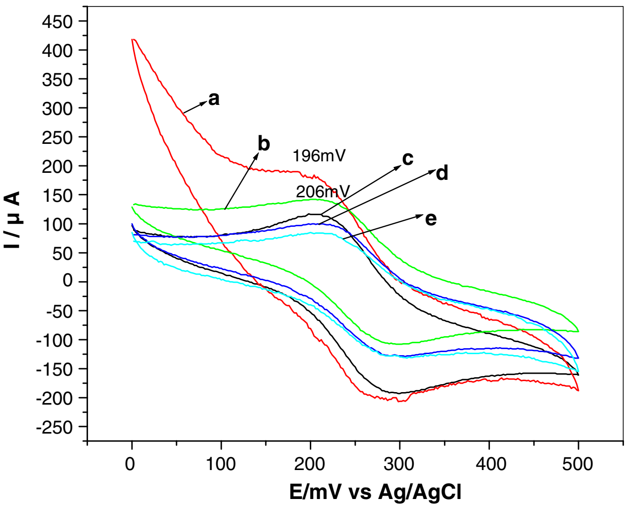


Fig. 3. Cyclic voltammograms of AYFc in aqueous solution of different pH value, pH 1 (a); pH 4 (b); pH 5 (c); pH 9 (d); pH 11 (e). Working electrode and auxiliary electrode: Pt disk. Reference electrode: Ag/AgCl (1 M KCl). Scan rate: 100 mV/s. Supporting electrode: NaCl aqueous solution (0.05 M).

To study the electrochemical stability of BSAFc and AYFc, their CVs were investigated in different pH media. Fig. 3 shows CVs of AYFc in aqueous solution of pH 1(a), 4(b), 5(c), 9(d) and 11(e), respectively, and Fig. 4 shows CVs of BSAFc in aqueous solution of pH 1(a), 4(b), 7(c), 9(d) and 13(e), respectively. The normal pH value of aqueous solution of BSAFc is 4. Herein, we adjust pH value of BSAFc solution from 4.0 to 1.0 using hydrochloric acid and from 4.0 to 13.0 using NaOH solution. Theoretically speaking, the half-wave potential of BSAFc should be constant in different pH media because $H^+$ or $OH^-$ does not participate in the redox reaction. However, it is found from Fig. 4 that the redox potentials of BSAFc changed at different pH conditions. The half-wave potential of BSAFc recorded at pH 1 shifts 20 mV to more negative than that at pH 4, and the peak current is larger than that at pH 4, which can be attributed to the formation of ion pair [11]. The ferrocene group of BSAFc becomes ferrocenium cation ($Fc^+$) upon oxidation and can easily form ion pair with $Cl^-$ existing in the solution. The half-potential of BSAFc becomes more negative and the electrochemical activity of it enhances with the increase of concentration of $Cl^-$ [11]. Meanwhile, the CVs of BSAFc at pH 7 and 9 reveal the same half-wave potentials as that at pH 4, which is due to the same concentration of $Cl^-$ in these three solutions and the difficulty of the interaction of $OH^-$ and $Fc^+$ to form ion pair. In the other words, there is almost no influence of concentration of $OH^-$ on the half-wave potential of BSAFc. When the concentration of $OH^-$ is increased to that at pH 13, the whole CV curve moves downwards, which may be the result of electrical catalytic activity of BSAFc. The pH value of normal AYFc aqueous solution is 4 and also is adjusted from 4.0 to 1.0 using hydrochloric acid and from 4.0 to 11.0 using NaOH solution. The CVs of AYFc showed in Fig. 3 display similar behavior to that of BSAFc. The half-wave potential of AYFc at pH 1 shifts 6 mV to more negative than that at pH 4 and then holds the line when the concentration of $OH^-$ increases at the constant concentration of $Cl^-$. This experimental result confirms the aforementioned discussion that concentration of $OH^-$ has little impact on the half-wave potential.

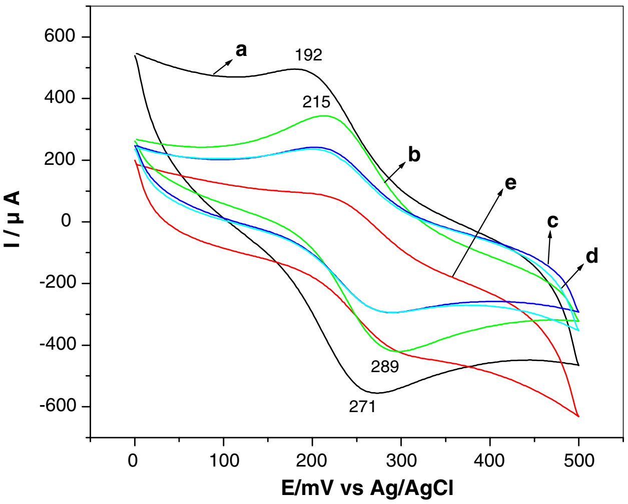


Fig. 4. Cyclic voltammograms of BSAFc in aqueous solution of different pH value, pH 1 (a); pH 4 (b); pH 7 (c); pH 9 (d); pH 13 (e). Working electrode and auxiliary electrode: Pt disk. Reference electrode: Ag/AgCl (1 M KCl). Scan rate: 100 mV/s. Supporting electrode: NaCl aqueous solution (0.05 M).

In conclusion, two new water-soluble functional ferrocene derivatives with sulfonic groups and/or azo structure were synthesized conveniently in aqueous media. The preparation process is quite simple and environment friendly. The electrochemical activities of BSAFc and AYFc firmly rely on the anion existing in the solution, especially the type of anion. For the two new ferrocene derivatives, they should be of potential application in development of new functional materials because of their redox and optical properties and further studies on their utilization in the preparation of conductive polymers with ferromagnetic property are underway and will be reported in due course.

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