Synthesis and Electrochemical Properties of Phloroglucin-Based Ferrocenyl Compounds and Their Application in Anion Recognition

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ABSTRACT: Phloroglucin-based ferrocenyl compounds, including hyperbranched phloroglucin-based ferrocenyl polymer and phloroglucin-based ferrocenyl dendrimer (Generation0), were prepared by a convenient approach. Cyclic voltammograms were used to investigate their electrochemical properties, and we found that the scanning rate and solvent had remarkable effects on electrochemical behavior of the compounds. These compounds showed electrochemical responses to the anions, and a selective recognition for $H_2PO_4^-$ over other anions was observed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1539–1546, 2008

Key words: dendrimers; electrochemistry; hyperbranched

INTRODUCTION

Compounds containing ferrocene, especially ferrocenyl dendritic compounds, have attracted increasing interest because of their unique properties.[1–3] Of all of their properties, the electrochemical properties of the ferrocenyl compounds is of particular interest because electrochemical studies are helpful in disclosing the redox properties of novel materials and the mechanism of the electrode process, which are important in the development of electrochemical sensors and modified electrodes.[4–6]

Anion recognition is an important topic in supramolecualr chemistry and has become a very active research area because of the universal existence of anions in biological systems and the environment.[7] Recently, great interest has been focused on the design of new host materials for anionic guests,[8] and various ferrocene-based compounds used as anion receptors have been reported.[9–11] Among these receptors, ferrocenyl dendrimers have received special attention because of their reversible electrochemical behavior, high sensitivity and selectivity to anions, and their stability on the electrode surface.[12–16] Hydrogen-bond donor groups, such as amide, urea, and thiourea groups, have been used most widely as the anion-binding units in anion receptors. However, few examples of ester-group-containing compounds used as anion receptors have been reported. In this study, we designed two kinds of ester-group-containing compounds, namely, ferrocene-based hyperbranched polymer (FBHP) and ferrocenyl dendrimer. These dendritic compounds were expected to serve as supramolecular receptors for anion recognition. The effects of molecular structure, potential scanning rate, and solvent on the electrochemical properties of compounds were investigated, and the anion recognition properties of the two compounds were also compared.

EXPERIMENTAL

Materials

Dichloromethane was dried over molecule sieves. Tetrahydrofuran (THF) was dried over molecule sieves and distilled from a Na/K alloy before use. NEt₃ was dried over molecule sieves. Ferrocenecarbonyl acid was used as received. 1,1′-Dichlorocarbonylferrocene and chlorocarbonylferrocene were synthesized according to a method from the literature.[17]

Synthesis of FBHP (compound 1)

Phloroglucin (0.29 g, 2.3 mmol) and ferrocene-1,1′-dicarboxylic chloride (0.72 g, 2.3 mmol) were charged into a three-necked glass reactor equipped with a gas inlet pipe for argon addition and a con-

denser with a vacuum adapter. THF (20 mL) was added to the reactor, followed by 0.5 mL of NEt$_3$. The reaction mixture was stirred at room temperature for 2 h and then refluxed for 20 h. The solution was washed with a saturated aqueous solution of Na$_2$CO$_3$ and then with distilled water, dried over MgSO$_4$, and filtered. After the solvent was removed *in vacuo*, compound **1** was obtained as a brown powder.

Yield: 0.68 g (81%). ^{1}H-NMR (δ, CDCl$_3$, 400 MHz): 7.07 (Ph—H), 4.55–5.02 (protons from ferrocene rings). Number-average molecular weight: 1379. Weight-average molecular weight/number-average molecular weight: 1.49.

Synthesis of the ferrocenyl dendrimer (compound 2)

A mixture of phloroglucin (0.14 g, 1.1 mmol), chlorocarbonylferrocene (0.85 g, 3.4 mmol), and NEt$_3$ (0.5 mL) in THF (25 mL) was stirred in argon as described previously. The crude product was purified by column chromatography (silica, CH$_2$Cl$_2$/MeOH = 9:1), which produced **2** as an orange powder.

Yield: 0.61 g (81%). ^{1}H-NMR (δ, CDCl$_3$, 400 MHz): 7.02 (s, 3H, Ph—), 4.99 (s, 2H, ferrocene (Fc)—H), 4.54 (s, 2H, Fc—H), 4.33 (t, 5H, Fc—H).

Instruments and reagents

^{1}H-NMR spectra were recorded with an Avance DMX-500 NMR spectrometer (Bruker Biospin Corp., Billerica, MA) with tetramethylsilane as an internal standard at room temperature. Gel permeation chromatography measurements were carried out on a Waters (Waters Corporation, Milford, MA) 201 instrument with a μ-Styragel column and THF as an eluent, and the molecular weight was calibrated with standard polystyrene. The cyclic voltammogram (CV) measurements were carried out with a CHI-630A electrochemical analyzer (CH Instruments, Inc., Austin, TX) in an undivided three-electrode cell. All electrodes were from CH Instruments. The platinum wire counterelectrode was a Teflon-shrouded platinum disk electrode ((diameter) Φ = 2 mm, geometric area = 0.0314 cm^2) that was polished to a mirror finish with a 0.05-μm Al$_2$O$_3$ paste on felt and cleaned by ultrasonication successively in 0.1M NaOH, 1 : 1 HNO$_3$/anhydrous ethyl alcohol, and double-distilled water. Then, it was dried and used for electrochemical measurement. The solutions were filtered with a 0.45-μm microbore filter and purged for 15 min with prepurified nitrogen before the measurements. CVs were obtained with an organic solution containing [n-Bu$_4$N][BF$_4$] (0.1M) as the supporting electrolyte, and the concentration of the ferrocenyl compound was 0.5 mM ferrocene unit. iR compensation was applied to all voltammogram measurements.

General method for the anion sensing experiments

The dichloromethane solution of [n-Bu$_4$N][BF$_4$] (0.1M) and ferrocenyl compound ([Fe] = 0.5 mM) was introduced into the electrochemical cell that contained the working electrode, reference electrode, and counterelectrode. The CV of the compound alone was recorded. Then, the anions were added as the n-Bu$_4$N$^+$ salts by small quantities with a microsyringe. After each addition, a CV was recorded.

## RESULTS AND DISCUSSION

Synthesis of the phloroglucin-based ferrocenyl compounds

Dendritic compounds, including hyperbranched polymer and phloroglucin-cored dendrimer (Generation0), were prepared. The synthetic routes are summarized in Scheme 1. FBHP was synthesized on the basis of a one-pot method, and a moderate yield was obtained. FBHP was characterized by ^{1}H-NMR spectroscopy. The broad peak for the cyclopentadienyl (Cp) ring in the range of δ = 4.77–5.10 indicated the existence of a different chemical environment for the ferrocene units in the molecule, and a single peak related to the protons of the Ph ring at δ = 7.16 demonstrated the successful reaction between phloroglucin and 1,1′-dichlorocarbonylferrocene. Phloroglucin-cored ferrocenyl dendrimer (compound **2**) was also synthesized, and its ^{1}H-NMR spectrum is shown in Figure 1.

Electrochemical behavior of the compounds

CV behavior of FBHP and phloroglucin-cored ferrocenyl dendrimer

CVs of FBHP (compound **1**) and phloroglucin-cored ferrocenyl dendrimer (compound **2**) were investigated in various solvents. Typical CVs of the two compounds in CH$_2$Cl$_2$ are shown in Figure 2. Single irreversible redox waves were observed at $E_{1/2}$ (half-wave potential in voltammetry) = +1.1675 V and +0.9295 versus Ag/Ag$^+$, corresponding to compound **1** and **2** respectively. The unicity of the ferrocene wave indicated that the electrostatic interaction between the multiple ferrocene units was weak.[14] Compared to the CV of the dendrimer, the peak potential of FBHP was more positive, the peak-to-peak separation (ΔE_p) of FBHP was larger, the peaks of FBHP were broader, and the oxidation currents (i_{pa}'s) were smaller. We noticed that the structure of the compounds had an influence on the electron-transport characteristics of the solution; namely, the rigid moiety phloroglucin units in FBHP may have prevented the electron-transfer process, and thus, it was more difficult for FBHP to be oxidized than for the dendrimer.
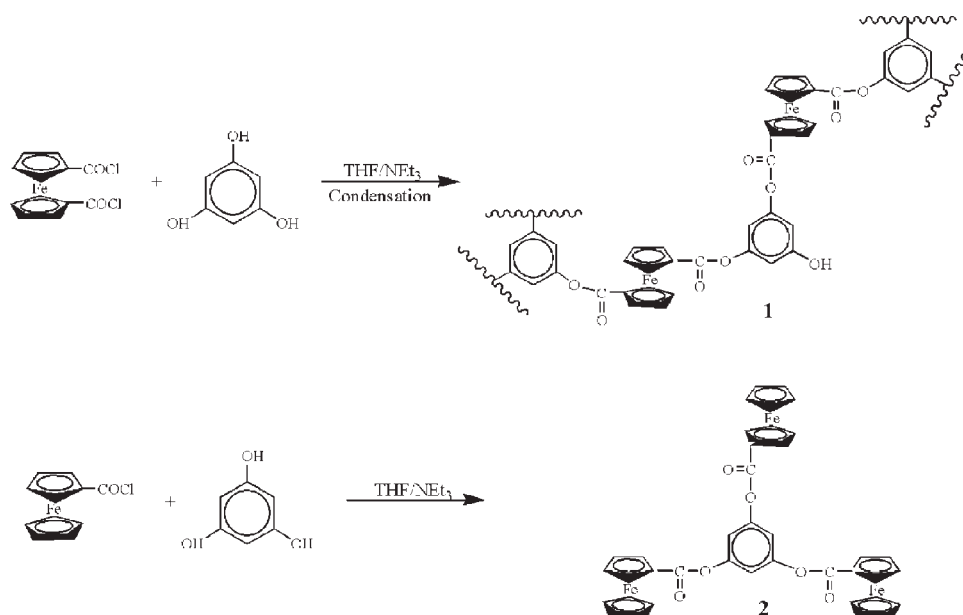
Scheme 1 Reaction scheme for the synthesis of the FBHP (compound **1**) and ferrocenyl dendrimer (compound **2**).

Influence of the scanning rate

The CVs of the two compounds at different potential scanning rates were investigated in CH_2Cl_2 solution, and the results are shown in Figure 3. The oxidation potentials of the two compounds were nearly constant, whereas the reduction potentials shifted to a positive position; thus, ΔE_p decreased with increasing scanning rate. Also, the increase in the reduction peak currents (i_{pc}'s) was faster than that of the i_{pa}'s, and the ratio i_{pc}/i_{pa} departed from 1 with increasing potential scanning rate. These indicated that the two compounds showed quasireversible electrochemical behavior at low scanning rates and irreversible behavior at high scanning rates.[4,18]

According to CV theory,[4,18] there is a linear relationship between the peak currents and the square root of the scanning rate for a totally irreversible process; the results of the linear correlation between i_p and $v^{1/2}$ are listed in Table I. On the other hand,
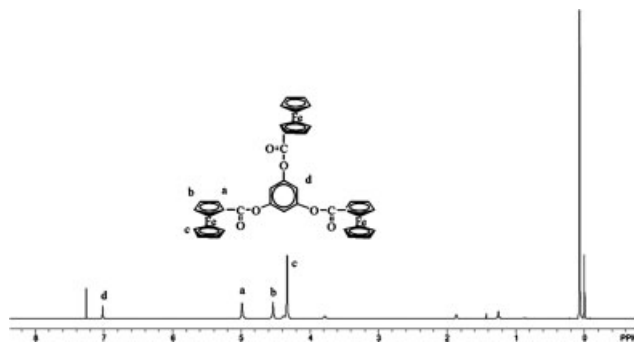
there is also a linear relationship between the peak potential [$E_p - E^{0'}$, where $E^{0'} = (E_{pc} + E_{pa})/2$; where E_p is peak potential, $E^{0'}$ is apparent formal potential, E_{pc} is cathodic peak potential, and E_{pa} is anodic peak potential] and the logarithm of the scanning rate for an absolutely irreversible process. Figure 4 shows the relationship between the peak potential and the scanning rate, which indicated that the electrochemical processes were complex; that is, the processes were neither simply reversible nor totally irreversible ones.[4] We presumed that the electrode process was diffusion controlled and obeyed Fick's
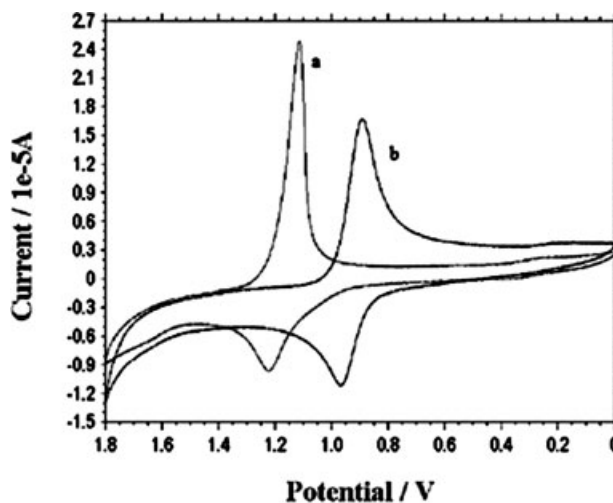

Figure 2 CVs of (a) compound **1** and (b) compound **2** (solvent = CH_2Cl_2, [Fe] = 0.5 mM, reference electrode = Ag/Ag$^+$, working electrode and counterelectrode = Pt, supporting electrolyte = 0.1M n-Bu$_4$NBF$_4$, scanning rate = 600 mV/s at 25°C).
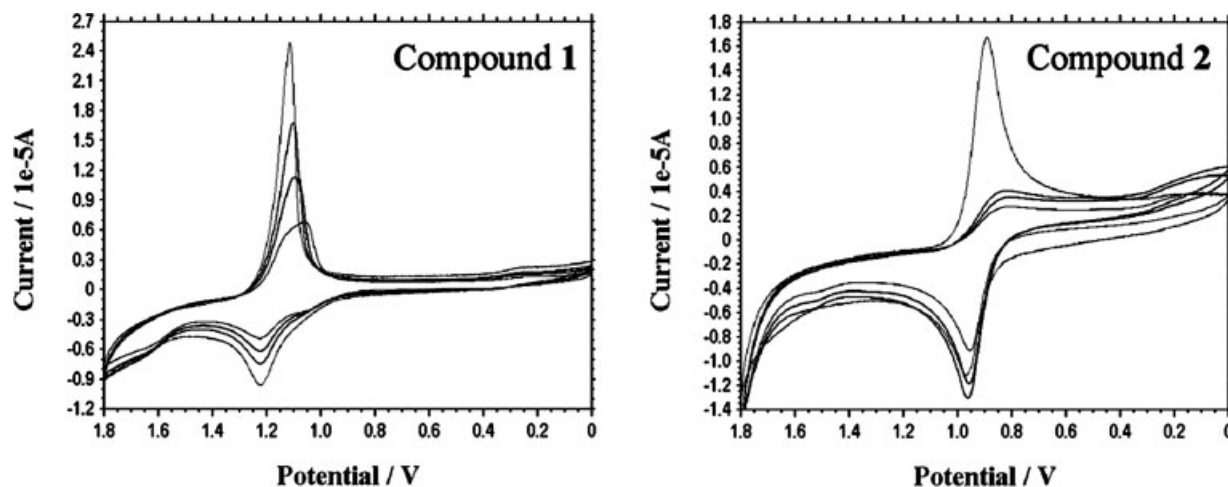

Figure 1 ^{1}H-NMR spectrum of compound **2**.

Figure 3 CVs of compounds **1** and **2** (solvent = CH_2Cl_2, [Fe] = 0.5 mM, reference electrode = Ag/Ag$^+$, working electrode and counterelectrode = Pt, supporting electrolyte = 0.1M n-Bu$_4$NBF$_4$, scanning rates = 200, 300, 400, and 600 mV/s from inner to outer at 25°C).

law. However, the rates of electron transport between the solution and the electrode were rather slow, which showed a relatively more remarkable influence on electrode behavior at higher scanning rates.[4,5]

Influence of the solvent

CVs of compounds **1** and **2** recorded in different solvents are shown in Figure 5. The solvent had a remarkable effect on the electrochemical behavior of the two compounds. In CH_2Cl_2, the difference between the oxidation potential and the reduction potential for these compounds were both larger than 60 mV, which indicated a slow heterogeneous electron-transfer process.[19] In THF, the potential difference (ΔE) became even larger. This may have been related to the dielectric constant and polarity of the solvent: in moderately polar solvent, the electron-transfer rate increased with increasing polarity, which made ΔE smaller in CH_2Cl_2 (dielectric constant = 9.1) than in THF (dielectric constant = 7.6). In the weak polar solvent 1,4-dioxane (1,4-DXO), the charge transport was not so effective, which caused

the redox peaks to be inconspicuous. In strong polar solvents, such as dimethylformamide and dimethyl sulfoxide (DMSO), the high dielectric constant caused a stabilizing effect on ferrocinium ions, which made it more difficult to be reduced. These phloroglucin-based ferrocene dendritic compounds exhibited similar electrochemical behavior to Jiang's[19] trimethylolpropane based hyperbranched polymers.

Electrochemical recognition of anions

Ferrocenyl compounds containing anion binding sites have been widely studied because of their potential application in anion recognition.[20] To achieve an ideal signaling output upon anion complexation for a ferrocene-based receptor, the electroactive unit ferrocene should be conjugated with the anion binding sites (usually amide or urea groups). The binding of the anion effectively stabilizes the positive charge of the ferrocinium, which causes the redox couple to shift to more negative potentials ($\Delta E_{1/2}$ (difference in half-wave potential in voltammeter for two couples) < 0).[8,21] This potential shift can be detected by electrochemical techniques.

TABLE I
Relationships Between the Peak Currents and Peak Potential (or Potential Scanning Rates) of the Compounds

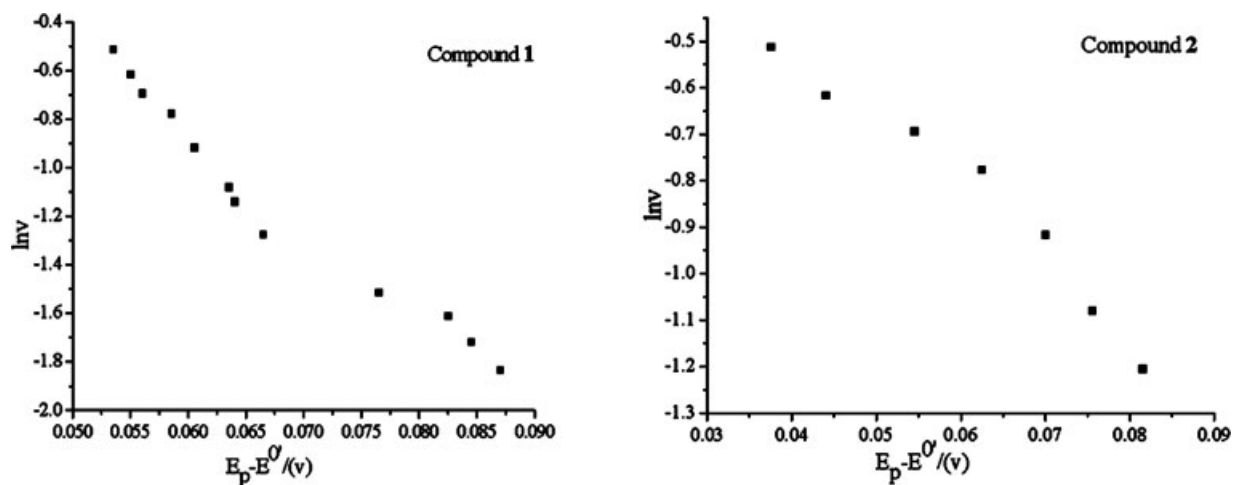| Compound	Rate range (V/s)	Linear equation	Correlation coefficient
1	0.02–0.3	$i_{pa} = -0.26 + 4.44v^{1/2}$	0.9849
		$\ln i_{pa} = -9.97 - 42.62(E_p - E^{0'})$	−0.9974
	0.02–0.6	$i_{pc} = -2.07 + 5.90v^{1/2}$	0.9941
		$\ln i_{pc} = -7.93 - 50.86(E_p - E^{0'})$	−0.9923
2	0.02–0.3	$i_{pa} = -0.06 + 2.15v^{1/2}$	0.9725
		$\ln i_{pa} = -11.92 + 9.26(E_p - E^{0'})$	0.9700
	0.02–0.6	$i_{pc} = -6.86 + 16.74v^{1/2}$	0.9749
		$\ln i_{pc} = -10.90 - 23.27(E_p - E^{0'})$	−0.9914

Figure 4 Peak potential of compounds **1** and **2** versus the potential scanning rate.

However, we were curious about whether the ester groups of compounds **1** and **2** could act as anion binding sites. As discussed previously, stable and reproducible CVs could be recorded in CH_2Cl_2 and THF, but the insolubility of n-Bu_4N^+ salts in THF precluded a detailed analysis of the anion bind-
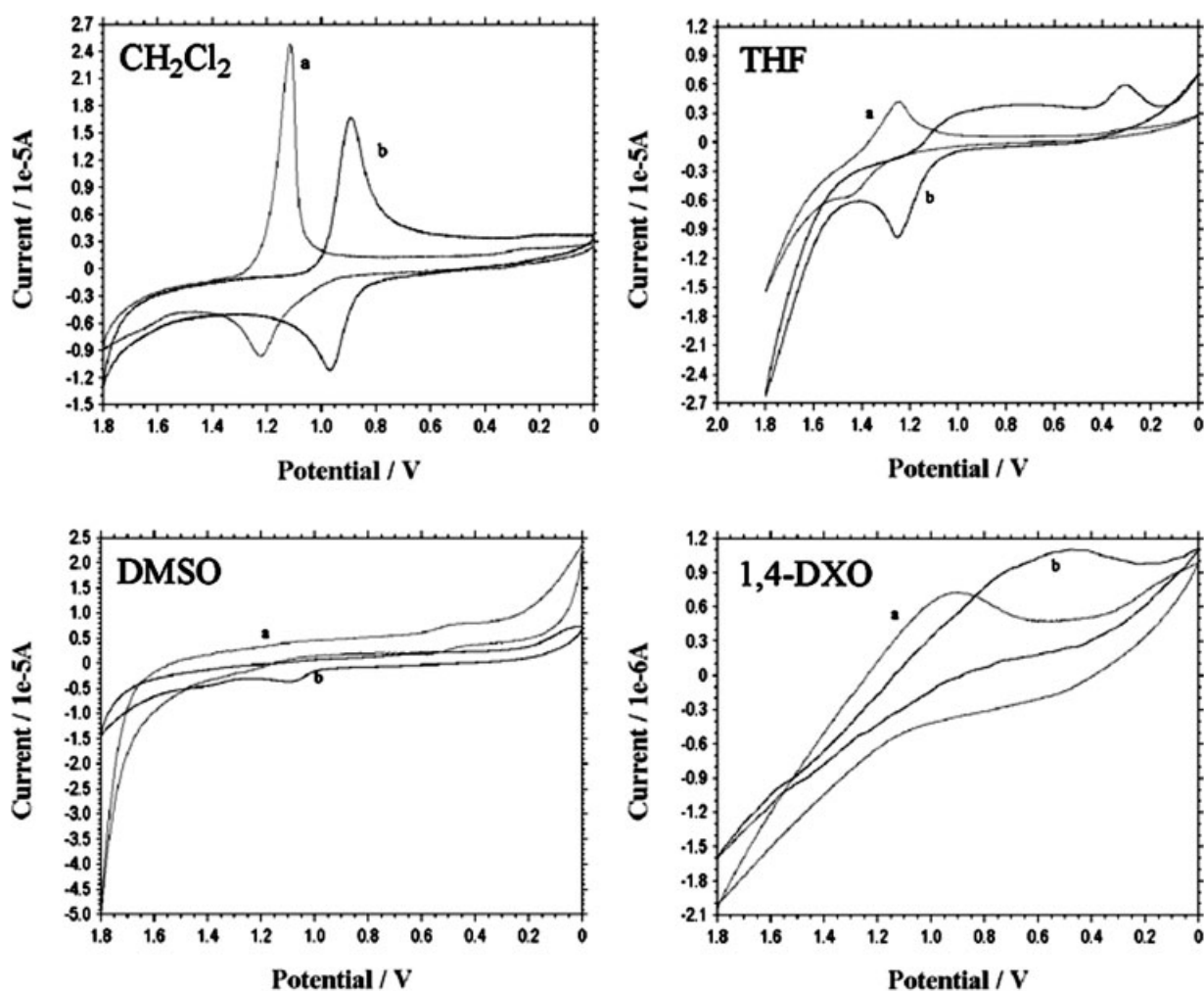

Figure 5 CVs of (a) compound **1** and (b) compound **2** in different solvents: CH_2Cl_2, THF, DMSO, and 1,4-DXO ([Fe] = 0.5 mM, reference electrode = Ag/Ag$^+$, working electrode and counterelectrode = Pt, supporting electrolyte = 0.1M n-Bu_4NBF_4, scanning rate = 600 mV/s at 25°C).
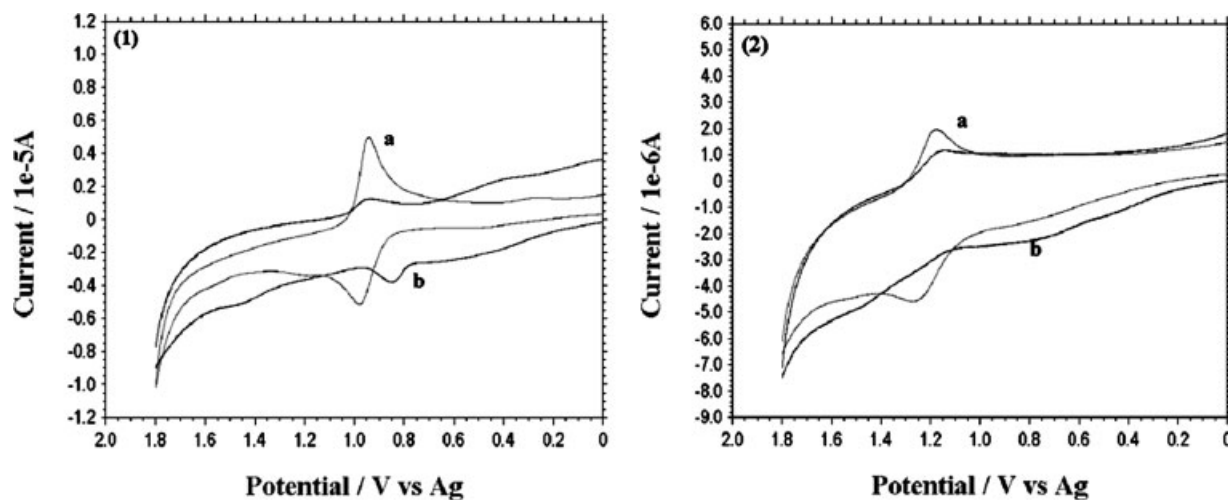
Figure 6 CVs of the dendrimer (compound **1**) and FBHP (compound **2**): (a) in the absence of $H_2PO_4^-$ and (b) in the presence of 1 equiv of $H_2PO_4^-$ per ferrocene center (solvent = CH_2Cl_2, [Fe] = 0.5 mM, working electrode and counterelectrode = Pt, supporting electrolyte = 0.1M n-Bu$_4$NBF$_4$, scanning rate = 100 mV/S at 25°C).

ing process in this solution. Therefore, electrochemical anion sensing experiments were carried out in CH_2Cl_2 solution.

Electrochemical response to the $H_2PO_4^-$ anion

It is significant to detect $H_2PO_4^-$ anion because of its important role in biological systems. The anion recognition properties of compounds **1** and **2** in CH_2Cl_2 solution was monitored by CVs, and the CVs obtained are shown in Figure 6.

The addition of increasing amounts of [n-Bu$_4$N][H$_2$PO$_4$] to the solution of compound **2** caused a decrease in the intensity of the initial redox wave along with the progressive appearance of a new oxidation wave at less positive potentials. After 1 equiv of $H_2PO_4^-$ per ferrocene center was added, the new wave reached full development. A new oxidation

wave appeared at a potential 142 mV less anodic than that of the initial wave; however, the reduction wave disappeared, which indicated an EC (heterogeneous electron transfer followed by homogeneous chemical reaction) mechanistic response to $H_2PO_4^-$ for compound **2**.[10,21,22] The full development of the new wave after the addition of approximately 1 equiv of $H_2PO_4^-$ reflected a one-to-one strong interaction between the receptor and the anion (Scheme 2).[13] According to the Kaifer–Echegoyen model,[8,23] the ratio K^+/K^0 (where K^+ and K^0 are the combination constants of the anion with the oxidized and reduced state, respectively) can be obtained with the following equation: $\Delta E = (RT/nF) \ln(K^+/K^0)$. For compound **2**, this ratio was about 255, which meant that it was 255 times more difficult for the receptor to bind the anion in the reduced state than in the oxidized state.
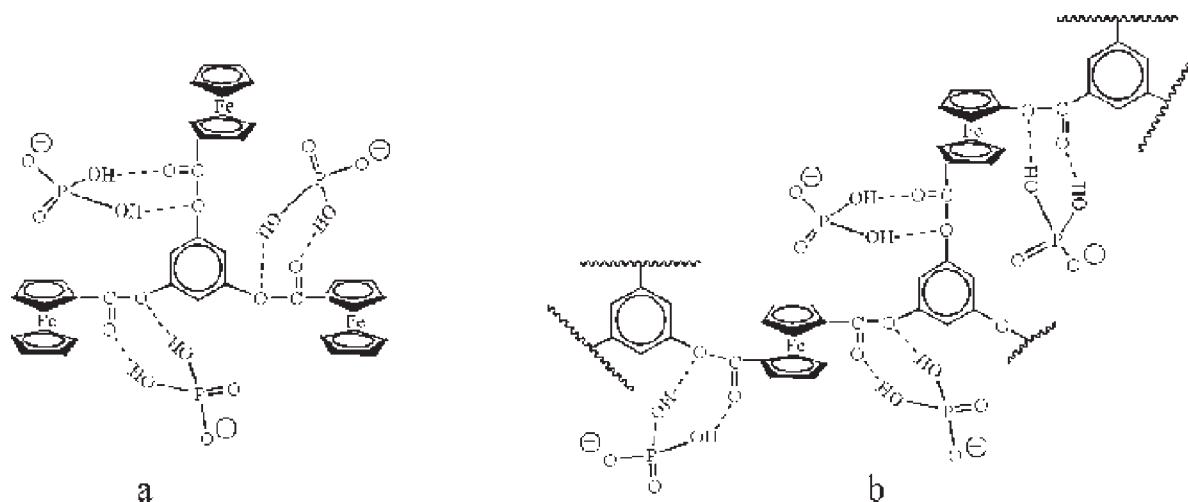
Scheme 2 One-to-one double hydrogen-bonding interactions between ester groups and $H_2PO_4^-$ anions.

TABLE II
Potential Shift $\Delta E_{1/2}$ Observed by the Fe$^{II/III}$ Redox System upon the Addition of Various n-Bu$_4$N$^+$ Salts^a

Compound	$\Delta E_{1/2}$ (mV)		
	$H_2PO_4^-$	HSO_4^-	Br^-
1	—^{b}	41	21
2	142	59	30

^{a} See the legends to Figures 6 and 7 for the conditions.
^{b} The data were unobtainable because of the inconspicuous redox wave.

Different behavior was observed when [n-Bu$_4$N][H$_2$PO$_4$] was added to the solution of compound **1**. The peak currents decreased dramatically with the addition of anions, and the redox wave became inconspicuous. According to CV theory, $i = kAn^{3/2}D^{1/2}v^{1/2}c$.[14] The sudden intensity drop of the CV wave was related to the decrease of the diffusion coefficient (D), which indicated the formation of a large-size electroactive species [Scheme 2(b)]. The inconspicuous redox wave induced by H$_2$PO$_4^-$ precluded further analysis of the recognition properties; thus, the dendrimer showed an advantage over hyperbranched polymers where clean electrochemical behavior was concerned. This was attributed to the well-defined molecular structure and the unicity of the ferrocene units of the dendrimer. However, the results obtained also showed that in the design of a new anion receptor, amide and urea groups were both better binding sites than the ester group in terms of binding strength.

Selectivity of the anion receptor

Of particular interest in the development of anion sensors is the selectivity of the anion receptor,[8] and elec-trochemical competition experiments were carried out by the addition of different anions. The potential shift induced by the anions is listed in Table II. The addition of [n-Bu$_4$N][HSO$_4$] led to different behavior of the Fc/Fc$^+$ couple in the case of H$_2$PO$_4^-$. A new wave was not observed, with only the initial wave shifted to a less positive potential, and the potential shift caused by HSO$_4^-$ was smaller (ca. 59 mV) than that by H$_2$PO$_4^-$. The addition of Br$^-$ anion induced similar behavior to HSO$_4^-$, except that the potential shift was even smaller (Fig. 7). The CV recorded by the addition of H$_2$PO$_4^-$ to the solution of compound **2** in the presence of an excess amount of HSO$_4^-$ and Br$^-$ (Fig. 8) was quite similar to that recorded in the presence of H$_2$PO$_4^-$ alone. These results indicate that compound **2** displayed the selectivity trend H$_2$PO$_4^-$ > HSO$_4^-$ > Br$^-$; namely, the receptor bound with H$_2$PO$_4^-$ much more strongly than with HSO$_4^-$, which was consistent with the increasing basicity order of the anions.

The carbonyl groups of these two receptors were electron-withdrawing groups. According to Kochi,[24] anion–π interactions may exist between the receptor and the anion, and a ultraviolet–visible spectral change may be observed upon the addition of anions. However, only a slight change was observed when H$_2$PO$_4^-$ and Br$^-$ anions were added into the solution of compounds **1** and **2**, which indicated weak anion–π interactions in these systems.

CONCLUSIONS

Phloroglucin-based ferrocenyl compounds were prepared by condensation reactions. Both the compounds exhibited quasireversible electrochemical behavior at low scanning rates and irreversible behavior at high scanning rates. The solvent had a remarkable effect on the electrochemical behavior of
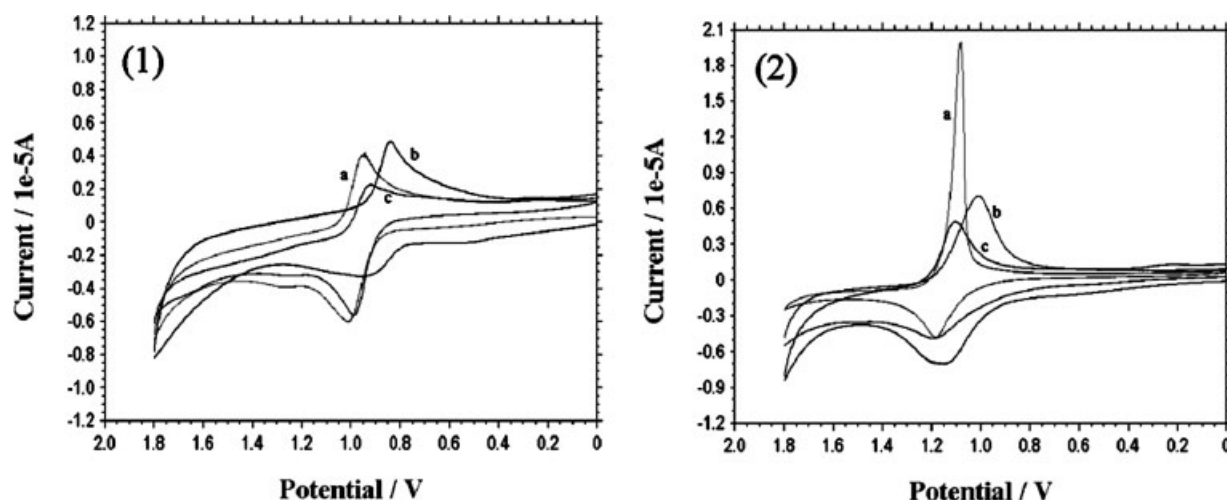

Figure 7 CV of compounds **1** and **2**: (a) receptor only, (b) receptor and 1 equiv of HSO$_4^-$, and (c) receptor and 1 equiv of Br$^-$ (solvent = CH$_2$Cl$_2$, [Fe] = 0.5 mM, reference electrode = Ag/Ag$^+$, working electrode and counterelectrode = Pt, supporting electrolyte = 0.1M n-Bu$_4$NBF$_4$, scanning rate = 100 mV/S at 25°C).
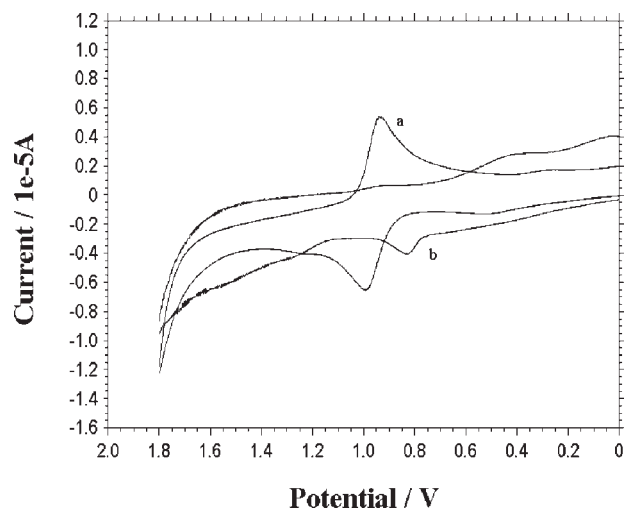
Figure 8 CV of compound **2**: (a) in the absence of anions and (b) in the presence of 1 equiv of $H_2PO_4^-$ per ferrocene center and an excess of HSO_4^- and Br^- (solvent = CH_2Cl_2, [Fe] = 0.5 mM, reference electrode = Ag/Ag$^+$, working electrode and counterelectrode = Pt, supporting electrolyte = 0.1M n-Bu$_4$NBF$_4$, scanning rate = 100 mV/S at 25°C).

FBHP, and a redox wave was only observed in moderately polar solvents. The ester groups of the compounds provided access to bind the anions, and thus, the compounds showed electrochemical responses to the anions: a new redox wave at a negative position replaced the initial wave after the addition of $H_2PO_4^-$ anions to the solution of the dendrimer. The phloro-glucin-cored dendrimer exhibited selectivity for $H_2PO_4^-$ over other anions, and the dendrimer was shown to be superior to the hyperbranched analogues in terms of cleaner electrochemical behavior for anion recognition. Therefore, compound **2** represents a novel candidate for anion sensors.

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