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Synthesis and electrochemical properties of calix[4]arene derivatives containing ferrocene units in the *cone* and *1,3-alternate* conformation

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ARTICLE INFO

ABSTRACT

Two novel calix[4]arene receptors containing ferrocene units in *cone* (L_1) and *1,3-alternate* (L_2) conformations have been synthesized from 25,27-dihydroxy-26,28-bis[(3-aminopropyl)oxy]calix[4]arene **4** or 25,26,27,28-tetra[(3-aminopropyl)oxy]calix[4]arene **6** and ferrocenecarboxaldehyde via condensation, respectively. Their structures have been characterized by ^{1}H, ^{13}C, APT, COSY NMR, FTIR, HSMR, and UV–vis spectral data. The electrochemical behavior of L_1 and L_2 has been investigated in the presence of F^-, Cl^-, Br^-, $H_2PO_4^-$, CH_3COO^- anions. Electrochemical studies show that these receptors electrochemically recognize CH_3COO^-, $H_2PO_4^-$, and Cl^-, anions. Using an UV–vis study, the selectivity to these anions in DMSO solution was confirmed.

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1. Introduction

Calixarenes represent one of the most important macrocyclic host molecules in supramolecular chemistry,[1,2] together with crown ethers[3] and cyclodextrins.[4] They are prepared by the base-catalyzed reaction of formaldehyde with phenol derivatives. Calixarenes have generated considerable interest as useful building blocks for the synthesis of hosts for cations, anions, and neutral molecules. During the last two decades, they have attracted much attention as receptors in supramolecular chemistry. The increasing interest in these compounds is stimulated by the simple large-scale synthesis of calixarenes, and the different ways in which they can be selectively functionalized at the narrow (phenolic groups) or at the wide rim (aromatic nuclei) (10–13). One of the most important features of these compounds is their diversity. Calixarenes find applications as selective binders and carriers, as analytical sensors, as catalysts and as model structures for biomimetic studies.[5–8]

Anion recognition and sensing is an increasingly important research topic in supramolecular chemistry due to the importance of various anions in biological and environmental locations. As a result of the importance of anions in a number of chemical and biochemical processes, the search for effective artificial molecular hosts is the subject of strong interest. Thus far, several different strategies have been used for anion complexation.[9–11] Basically, the receptors can be divided into two main groups: (i) charged systems exploring electrostatic interactions with positively charged species; (ii) neutral systems using other kinds of interactions, such as donor–acceptor interactions (receptors based on the Lewis acids), hydrogen bonds, hydrophobic effects, etc. Significant progress has been made, especially in the design and synthesis of neutral receptors based on hydrogen bonding interactions.[12] Supramolecular electrochemical recognition plays important role in the research fields of both supramolecular chemistry and electrochemistry.[13,14] In recent years, some research focused on using calixarenes as building blocks to construct redox-active calixarene derivatives.[15–17] To reach this aim, some calixarenes bearing ferrocene units were synthesized and their electrochemical recognition for guests was studied. For example, Beer and co-workers reported a series of ferrocene-functioned calixarenes.[18,19] Tuntulani and co-workers reported ferrocene-amide calixarenes with recognition for carboxylic anions.[20,21] Guo and co-workers reported a ferrocene-based thiacalix[4]arene ditopic receptor for europium(III) and dihydrogenphosphate ion.[22]

In the present work, we report the synthesis and characterization of two novel calix[4]arene Schiff base derivatives containing ferrocene units in the *cone* and *1,3-alternate* conformations and investigate their electrochemical behavior toward F^-, Cl^-, Br^-, $H_2PO_4^-$, and CH_3COO^- anions. The electrochemical investigation revealed that these compounds can respond to the anions with the different shifts of the Fc/Fc^+ couple; the selectivity toward CH_3COO^-, $H_2PO_4^-$, and Cl^- ions in DMSO solution was confirmed with the UV study.

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2. Results and discussion

2.1. Synthesis

This work is mainly focused on the synthesis and electrochemical application of calix[4]arene derivatives bearing ferrocene moieties. For the desired goal, two novel calix[4]arene Schiff base derivatives containing ferrocene groups were synthesized by using 25,27-dihydroxy-26,28-bis[(3-aminopropyl)oxy]calix[4]arene **4**, 25,26,27,28-tetra[(3-aminopropyl)oxy]calix[4]arene **6**, and ferrocenecarboxaldehyde as the precursors. The synthetic routes are shown in Schemes 1 and 2. *p-tert*-Butylcalix[4]arene **1**, calix[4]arene **2**, 25,27-bis[(3-phthalimidopropyl)oxy]calix[4]arene **3**, and 25,27-bis[(3-aminopropyl)oxy]calix[4]arene **4** were synthesized according to the reported literature procedure.[6,23] Compound **4** was refluxed with ferrocenecarboxaldehyde in CH_2Cl_2 and a catalytic amount of triethylamine to give the corresponding Schiff base derivative of calix[4]arene **L₁** in 85% yield. The preparation of 25,26,27,28-tetra[(3-iminoferrocenepropyl)oxy]-calix[4]arene **L₂** in the *1,3-alternate* conformation is depicted in Scheme 2. First, 25,27-bis[(3-phthalimidopropyl)oxy]calix[4]arene **3** was reacted with *N*-(3-bromopropyl)phthalimide in the presence of Cs_2CO_3 to give 25,26,27,28-tetra[(3-phthalimidopropyl)oxy]-calix[4]arene **5** in a 65% yield. Subsequently, the phthalimido groups in compound **5** were removed with hydrazine hydrate in EtOH to give 25,26,27,28-tetra[(3-aminopropyl)oxy]-calix[4]arene **6** in a 90% yield. Then, 25,26,27,28-tetra[(3-iminoferrocenepropyl)oxy]-calix[4]arene **L₂** was obtained by reacting compound **6** with ferrocenecarboxaldehyde in CH_2Cl_2 and a catalytic amount of triethylamine.
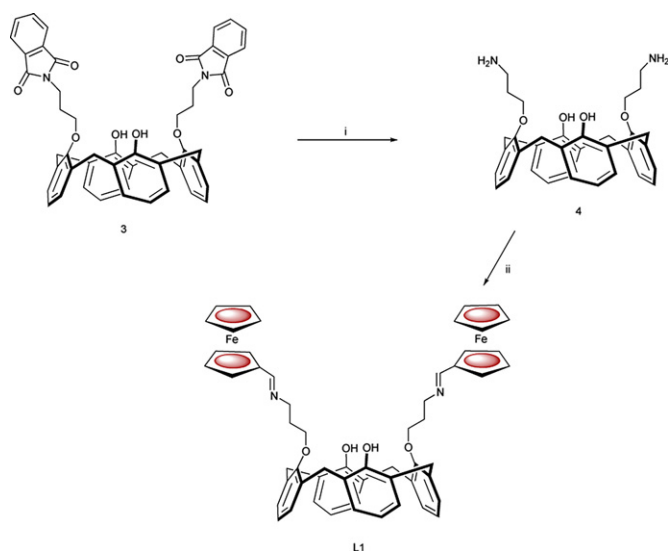
Scheme 1. Reagents and conditions: (i) $NH_2NH_2 \cdot H_2O$, C_2H_5OH; (ii) ferrocenecarboxaldehyde, triethylamine, CH_2Cl_2, 85%.

The new compounds **5**, **6**, **L₁**, and **L₂** were characterized by a combination of FTIR, ^1H, ^{13}C and APT, COSY NMR, and elemental analysis. The formation of Schiff base derivatives of calix[4]arene **L₁** and **L₂** was confirmed by the appearance of the characteristic HC=N bands at about 1643 and 1640 cm^{-1} in their FTIR spectra, and by the disappearance of the NH_2 band at 3368 and 3369 cm^{-1} in the FTIR spectra, respectively. The ^1H NMR spectra of **L₁** and **L₂** receptors are shown in Fig. 1. The synthesis of **L₁** and **L₂** receptors was also confirmed by the appearance of imine protons (HC=N) at 8.21 and 8.13 ppm in the ^1H NMR spectra. The conformational characteristics of calix[4]arenes were conveniently estimated by the splitting pattern of the $ArCH_2Ar$ methylene protons in the ^1H and ^{13}C NMR spectroscopy.
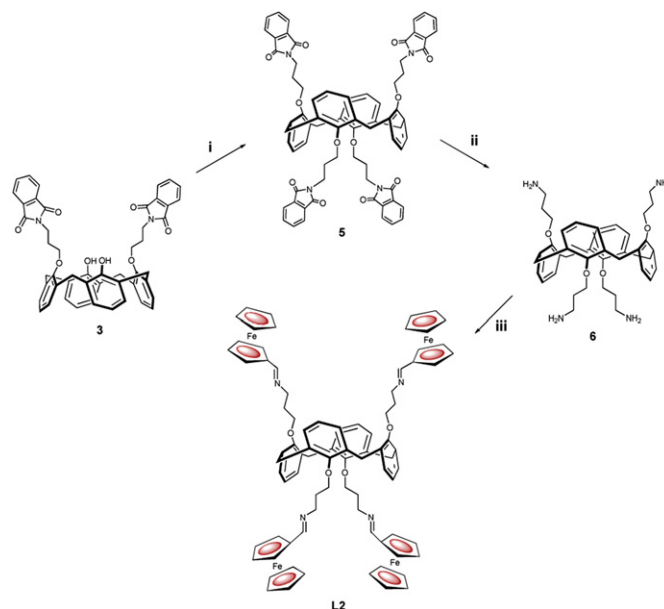
Scheme 2. Reagents and conditions: (i) *N*-(3-bromopropyl)phthalimide, Cs_2CO_3, MeCN, 65%; (ii) $NH_2NH_2 \cdot H_2O$, C_2H_5OH, 90% (iii) ferrocene-carboxaldehyde, triethylamine, CH_2Cl_2, 80%.
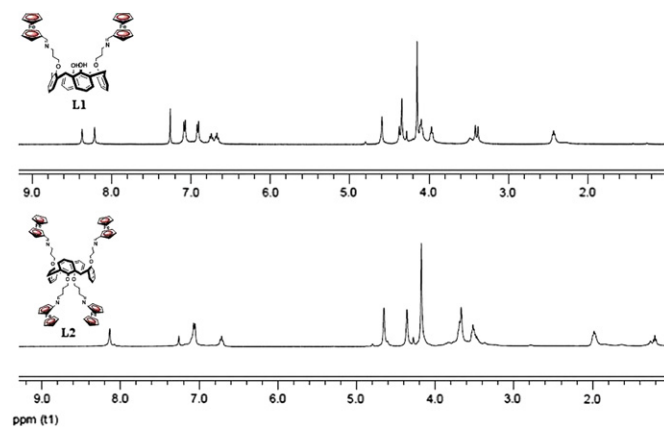

Fig. 1. ^1H NMR spectra of receptors **L₁** and **L₂** in $CDCl_3$ at 25 °C.

^1H and ^{13}C NMR data showed that **L₁** and **L₂** have a *cone* and *1,3-alternate* conformation, respectively. A typical AB pattern was observed for the methylene bridge $ArCH_2Ar$ protons at 3.40 and 4.36 ppm (J=13.4 Hz) in ^1H NMR for **L₁**. The *1,3-alternate* conformation of **L₂** was confirmed by the carbon absorption of the bridging methylene groups ($ArCH_2Ar$) of the calix[4]arene present at 36.7 ppm in the ^{13}C NMR and the singlet around 3.66 ppm in the ^1H NMR for the corresponding methylene hydrogens.[24]

2.2. Electrochemical anion sensing studies

Electrochemical data for the ferrocene substituted calix[4]arenes, **L₁** and **L₂** were obtained by cyclic voltammetry in DMSO solutions and were recorded in the anodic region (up to +1 V) showing distinct reversible oxidations stemming from the redox-active ferrocenyl substituents (Table 1, Fig. 2). In both cases the first ferrocenyl centered oxidations are shifted anodically by 26 and 101 mV in comparison to the parent compound ferrocene ($E_{1/2}$=515 mV, in DMSO). This can be plausibly rationalized by the electron withdrawing nature of the azomethine functionality, which renders the ferrocenyl part more difficult to oxidize.

Table 1
Cyclic voltammetric data in millivolts of 1.0 mM Ferrocene (red curve), **L₁** (blue curve), and **L₂** (black curve) at a glassy carbon (GC) working electrode, Pt gauze counter electrode and Ag/AgCl reference electrode in DMSO containing 0.1 M TBATFB in the potential range from 0.2 to +1 V with a scan rate of 200 mV s⁻¹.

Compound	E_{pa} (mV)	E_{pc} (mV)	$E_{1/2}$ (mV)	ΔE_p (mV)
Ferrocene	556	475	515	81
L₁	597	484	541	113
L₂	703	528	616	175

E_{pa} (anodic peak potential), E_{pc} (cathodic peak potential), $E_{1/2}=(E_{pa}+E_{pc})/2$, $\Delta E_p=E_{pa}-E_{pc}$.
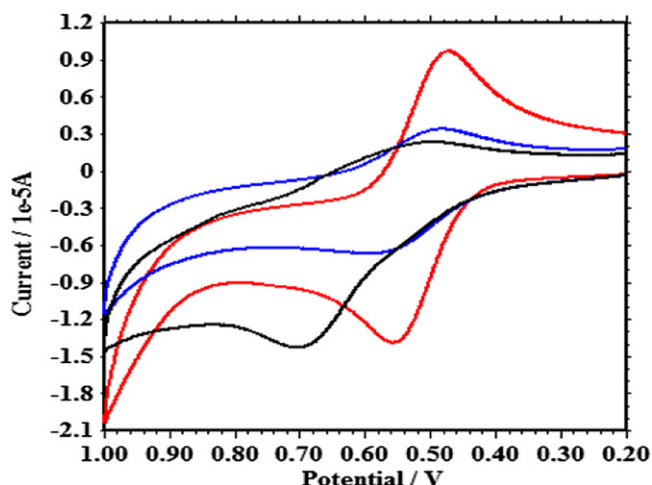
Fig. 2. Cyclic voltammograms recorded for the 1.0 mM Ferrocene (red curve), **L₁** (blue curve), and **L₂** (black curve) as the same conditions described in Table 1.

On the basis of the separation between the anodic and cathodic potentials (ΔE_p), and the plots of peak current versus the square root of the scan rates, which showed deviation from a straight line at higher scan rates, the couple was regarded as quasireversible for **L₁** and **L₂**. At different scan rates, the observation of only one redox wave for all iron centers in compounds **L₁** and **L₂** indicates no interaction between the ferrocene units (see Supplementary data).

In order to evaluate the potential electrochemical sensing capabilities of the novel compounds **L₁** and **L₂**, their voltammetric behavior was investigated toward the anionic species. Cyclic voltammetry was used to probe the changes in the redox potentials of the compounds upon complexation with anions. Titrations were carried out by addition of aliquots of tetrabutylammonium salts of F⁻, Br⁻, Cl⁻, CH₃COO⁻, and H₂PO₄⁻, followed by CV measurement at a scan rate of 100 mV/s. The addition of anions was generally varied from 0.2 to 4.0 equiv. As can be seen in Figs. 3 and 4, the progressive addition of CH₃COO⁻ and H₂PO₄⁻ ions to a solution of **L₁** and **L₂** resulted in a shift of the oxidation potential associated with the ferrocene units. The presence of 1.6 equiv of CH₃COO⁻ induced the decrease of the redox peak current of the receptor studied and its cathodic shift (Fig. 4a). Maximum displacement (ΔE, mV) in the first potential of the **L₁** receptor observed upon the addition of 1.6 equiv of the tetrabutylammonium salt of the CH₃COO⁻, H₂PO₄⁻ anions in DMSO as 45 mV and 35 mV, respectively. These results indicated that complexation of CH₃COO⁻ and H₂PO₄⁻ by the ferrocene functionalized calix[4]arene changed its redox properties. This could be the reason for the decrease of the peak current of the ferrocene/ferrocenium couple in the presence of anions.

In an effort to test for selectivity, CV titration experiments were also carried out with solutions containing F⁻, Cl⁻ or Br⁻ ions. However, in the presence of these anions the redox events did not

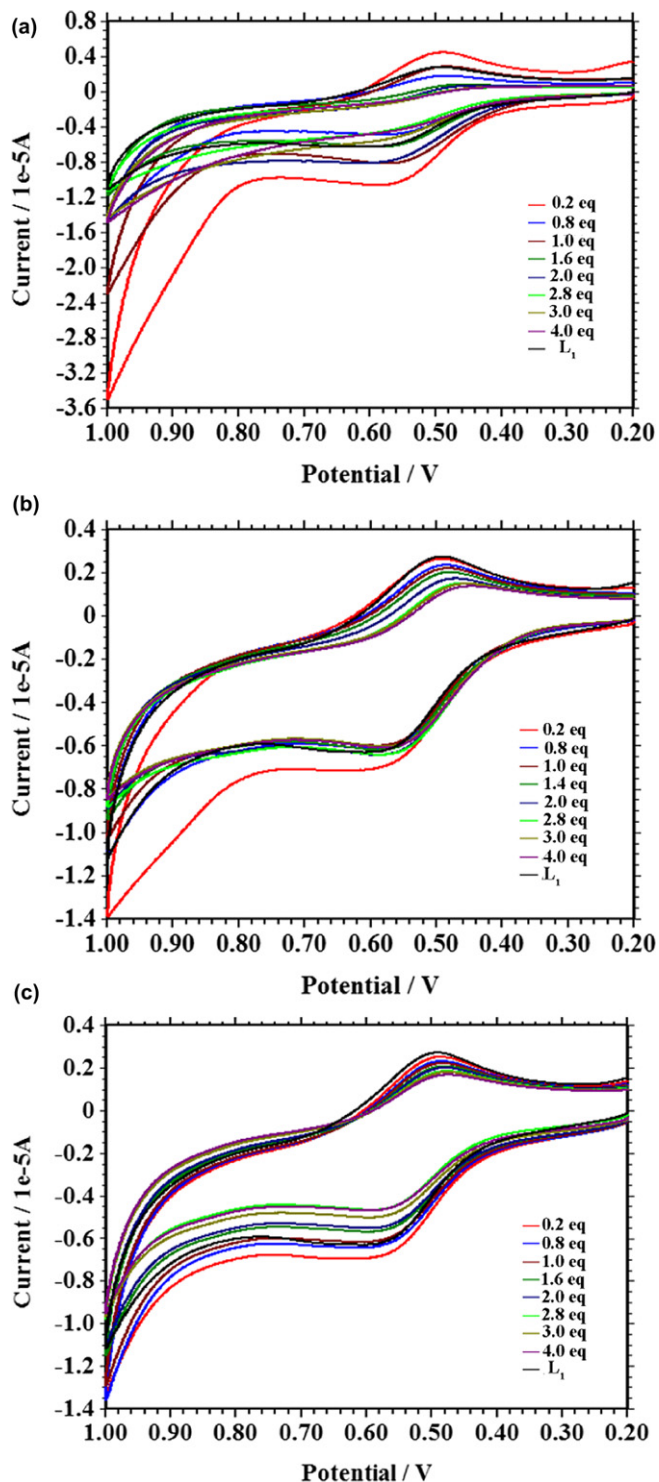**Fig. 3.** Titration of **L₁** and anions (CH₃COO⁻, H₂PO₄⁻, and Cl⁻) in DMSO with 0.1 M TBATFB and scan rate of 100 mV s⁻¹. (a) CH₃COO⁻, (b) H₂PO₄⁻, (c) Cl⁻.

result in the expected shift of the oxidation potential, meaning that no reliable results (or sensing effects) could be obtained for **L₁**. In the case of receptor **L₂** being 'titrated' with Cl⁻ ions, a decrease in the peak current of ferrocene/ferrocenium couple was observed after approximately two stoichiometric equivalents of Cl⁻ had been added. A similar decrease in peak current was observed in the ferrocene/ferrocenium couple (see Supplementary data) when receptor **L₂** was titrated with increasing amounts of either F⁻ or Br⁻ ions.
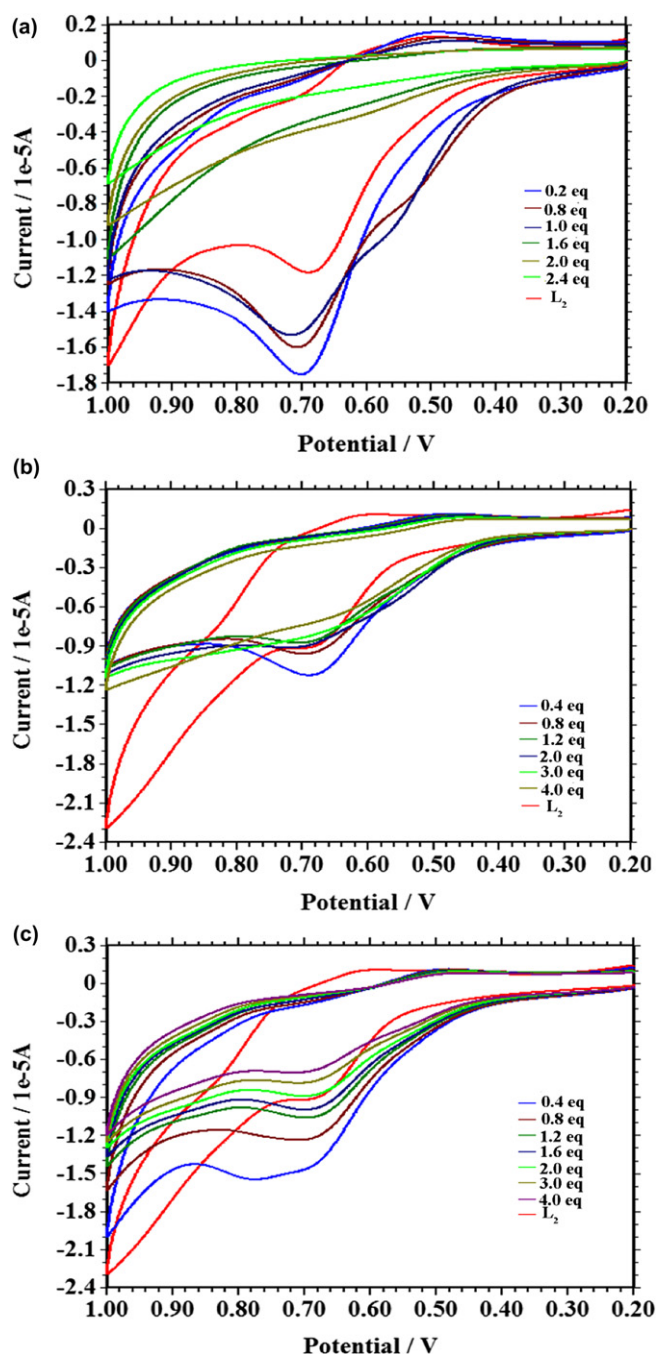
Fig. 4. Titration of L_2 and anions (CH_3COO^-, $H_2PO_4^-$, and Cl^-) in DMSO with 0.1 M TBATFB and scan rate of 100 mV s^{-1}. (a) CH_3COO^-, (b) $H_2PO_4^-$, (c) Cl^-.

2.3. UV studies

The anion binding properties of the receptors L_1 and L_2 were investigated using UV−vis spectroscopic titration in a DMSO solution. Various anions were taken as tetrabutylammonium (TBA) salts. The UV spectra of L_1 and L_2 showed a shoulder at 319 nm, apparently corresponding to the n→π* transition (non-bonding electrons of nitrogen to π* orbital of imine) and a weak band at 435 nm corresponding to the d−d transition for the iron of ferrocene. Upon the addition of increasing amounts of CH_3COO^-, $H_2PO_4^-$ or Cl^- anions to the solution of receptor L_2 ($1 \times 10^{4-}$ M), the intensity of the absorption peak at 435 nm (corresponding to the d−d transition of ferrocene of L_2) gradually increases and reaches

a maximum for the different concentrations of L_2 and CH_3COO^-, $H_2PO_4^-$ or Cl^- anions and then gradually decreases with the extra addition of CH_3COO^-, $H_2PO_4^-$ or Cl^- anions. The stoichiometries of the complexes formed between L_2 and CH_3COO^-, $H_2PO_4^-$ or Cl^- were determined by Job's method of continuous variation and were found to be 1:2, 1:1.8, and 1:1.6, respectively. The anion binding properties of L_1 were determined with a CH_3COO^- anion. The stoichiometry of the complex formed between L_1 and the CH_3COO^- anion was determined by Job's method and found to be 1:0.8. The UV−vis spectroscopic titrations for L_1 with the CH_3COO^- anion and for L_2 with the CH_3COO^-, $H_2PO_4^-$, and Cl^- anions indicate 1:1 and 1:2 binding-stoichiometry, respectively. Fig. 5 shows the Job plot and spectra of L_2 obtained during the titration with CH_3COO^- (see Supplementary data for the titration and Job plots analysis of CH_3COO^- with L_1 and $H_2PO_4^-$, Cl^- anions with L_2).
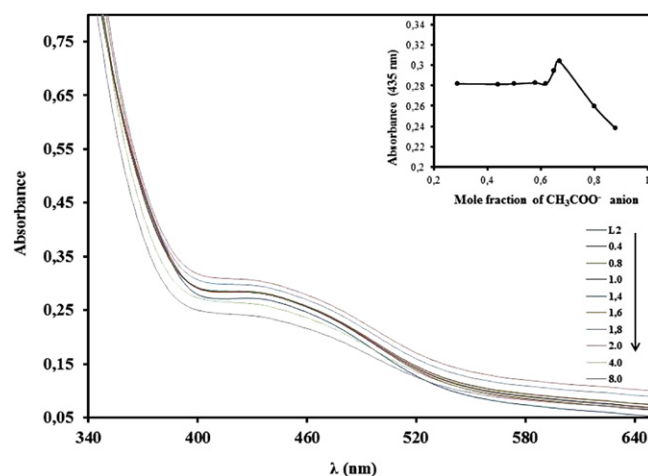

Fig. 5. Titration and Job plot of L_2 (10^{-4} M in DMSO) and CH_3COO^- anion.

3. Conclusion

In this study, novel anion receptors based on calix[4]arene and ferrocene have been synthesized and characterized using ^1H, ^{13}C, APT, COSY NMR, FTIR, and HRMS techniques. The electrochemical behaviors and UV−vis properties of these receptors were investigated in the presence of some anions. The electrochemical results showed that although L_2 has selectivity for all the anions studied, L_1 has better selectivities for CH_3COO^- and $H_2PO_4^-$ in comparison with other anions. Also, thus far, these results agree with the UV−vis titration in that two receptors recognize CH_3COO^- anion better than $H_2PO_4^-$, F^-, Br^-, and Cl^-. The UV−vis spectroscopic titrations for L_1 with CH_3COO^- anion and for L_2 with the CH_3COO^-, $H_2PO_4^-$, and Cl^- anions indicate 1:1 and 1:2 binding-stoichiometry, respectively.

4. Experimental

4.1. General

Melting points were determined on an Electrothermal 9100 apparatus in a sealed capillary and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at room temperature on a Varian 400 MHz spectrometer in $CDCl_3$. FTIR spectra were obtained on a Perkin Elmer Spectrum 100 FTIR spectrometer. UV/Vis spectra were measured with a Perkin Elmer Lambda 25 spectrometer. Elemental analyses were performed using a Leco CHNS-932 analyzer. Cyclic voltammetry was performed with a CHI 600C electrochemical

workstation (USA) in a conventional three-electrode electrochemical cell. Working electrode was a bare glassy carbon (GC) disk (BAS Model MF-2012) with a geometric area of 0.027 cm^2. A platinum wire and Ag/AgCl/KCl(sat.) electrode were used as the auxiliary and the reference electrode, respectively. GC electrode was polished with 1.0 and 0.05-μm α-Al$_2$O$_3$ powders successively and sonicated in DMSO for about 2 min after each polishing step. Analytical TLC was performed using Merck prepared plates (silica gel 60 F$_{254}$ on aluminum). Flash chromatography separations were performed on a Merck Silica Gel 60 (230–400 Mesh). All reactions, unless otherwise noted, were conducted under a nitrogen atmosphere. All starting materials and reagents used were of standard analytical grade from Fluka, Merck, and Aldrich and used without further purification.

4.2. Synthesis

As starting materials, *p-tert*-butylcalix[4]arene **1**, calix[4]arene **2**, 25,27-Bis[(3-phthalimidopropyl)oxy]calix[4]arene **3**, and 25,27-bis[(3-aminopropyl)oxy]calix[4]arene **4** were synthesized according to the reported literature procedure.[6,23]

4.2.1. 25,27-Bis[(3-iminoferrocenepropyl)oxy]-26,28-dihydroxy calix [4]arene *L₁*.
25,27-Bis[(3-aminopropyl)oxy]calix[4]arene **4** (1.0 g, 1.86 mmol) in CH$_2$Cl$_2$ (40 ml) was added to a stirred solution of ferrocenecarboxaldehyde (0,84 g, 3.91 mmol) and triethylamine (1 ml, excess) in CH$_2$Cl$_2$ (20 ml) and the mixture was stirred for 24 h under nitrogen. After evaporation of the solvent, the solid residue was washed with hexane twice to remove unreacted ferrocenecarboxaldehyde and dried in vacuum. Yield 85%; mp 178–180 °C; FTIR; 1643 cm^{-1} (CH=N); ^{1}H NMR (400 MHz, CDCl3): δ (ppm) 8.36 (s, 2H, ArOH), 8.21 (s, 2H, CHN), 7.07 (d, 4H, *J*=7.4 Hz, Ar*H*), 6.91 (d, 4H, *J*=7.4 Hz, Ar*H*), 6.74 (t, 2H, *J*=7.4 Hz, Ar*H*), 6.67 (d, 2H, *J*=7.4 Hz, Ar*H*), 4.59 (s, C$_5$*H*$_4$, 4H), 4.36 (d, 4H, *J*=13.1 Hz, ArC*H*$_2$Ar), 4.34 (s, C$_5$*H*$_4$, 4H), 4.15 (s, C$_5$*H*$_5$, 10H), 4.09 (t, 4H, *J*=5.6 Hz, OC*H*$_2$), 3.96 (t, 4H, *J*=5.7 Hz, NC*H*$_2$), 3.40 (d, 4H, *J*=13.1 Hz, ArC*H*$_2$Ar), 2.43 (p, 4H, *J*=5.6 Hz, OCH$_2$C*H*$_2$CH$_2$N); HRMS calculated for C$_{56}$H$_{54}$N$_2$O$_4$Fe$_2$: 930.7290. Found: 930.7310.

4.2.2. 1,3-Alternate-25,26,27,28-tetra[(3-phthalimidopropyl)oxy]-calix[4]arene **5**.
Compound **5** was synthesized using a modified procedure originally reported by Chrisstoffels and co-workers.[24] A solution of 25,27-Bis[(3-phthalimidopropyl)oxy]calix[4]arene **3** (1.0 g, 1.25 mmol), Cs$_2$CO$_3$ (1.6 g, 4.9 mmol), and *N*-(3-bromopropyl)phthalimide (2.0 g, 7.5 mmol) in dry MeCN (100 mL) was refluxed for 3 days. Then the solvent was removed under reduced pressure. Subsequently, the residue was dissolved in CH$_2$Cl$_2$ (70 mL) and washed with 1 N NH$_4$Cl (3×50 mL) and water (2×50 mL). The organic phase was separated, dried with MgSO$_4$, and evaporated to afford a solid, which was crystallized from MeOH to give **5** as a pure white powder. Yield 65%; mp 255–257 °C; FTIR; 1694 cm^{-1} (C=O); ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.79–7.65 (m, 16H, Ph*H*), 6.98 (d, 8H, *J*=7.4 Hz, Ar*H*), 6.82 (t, 4H, *J*=7.4 Hz, Ar*H*), 3.72 (s, 8H, ArC*H*$_2$Ar), 3.52 (t, 8H, *J*=7.2 Hz, NC*H*$_2$), 3.45(t, 8H, *J*=7.4 Hz, OC*H*$_2$), 1.59 (p, 8H, *J*=7.2 Hz, OCH$_2$C*H*$_2$CH$_2$N); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 168.3, 156.6, 134.0, 133.9, 132.4, 129.6, 123.2, 122.9, 68.4, 38.0, 35.4, 29.0; HRMS calculated for C$_{72}$H$_{60}$N$_4$O$_{12}$: 1173.2664. Found: 1173.2687.

4.2.3. 1,3-Alternate-25,26,27,28-tetra[(3-aminopropyl)oxy]-calix[4] arene **6**.
A solution of 25,26,27,28-tetra[(3-phthalimidopropyl) oxy]-calix[4]arene **5** (1.0 g, 0.85 mmol) and NH$_2$NH$_2$·H$_2$O (0.83 g, 17 mmol) in ethanol (50 mL) was refluxed at 110–120 °C for 16 h. Then the solvent was removed under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$ (30 mL) and washed with a solution of NH$_4$OH (pH ≈ 9) (3×15 mL). The organic phase was separated, dried

with MgSO$_4$, and evaporated to afford **6** as a pure solid. Yield 90%; mp 179–181 °C; FTIR: 3369 cm^{-1} (NH$_2$); ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.05 (d, 8H, *J*=7.8 Hz, Ar*H*), 6.80 (t, 4H, *J*=7.4 Hz, Ar*H*), 3.74 (s, 8H, ArC*H*$_2$Ar), 3.62 (t, 8H, *J*=6.8 Hz, NC*H*$_2$), 2.64 (t, 8H, *J*=6.8 Hz, OC*H*$_2$), 1.61 (p, 8H, *J*=6.8 Hz, OCH$_2$C*H*$_2$CH$_2$N). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 156.6, 133.8, 129.8, 123.7, 68.4, 39.9, 37.9, 34.1; HRMS calculated for C$_{40}$H$_{52}$N$_4$O$_4$: 652.8653. Found: 652.8677.

4.2.4. 1,3-Alternate-25,26,27,28-tetra[(3-iminoferrocenepropyl)oxy]-calix[4]arene *L₂*.
To a solution of 25,26,27,28-tetra[(3-aminopropyl) oxy]-calix[4]arene **5** (1.0 g, 1.53 mmol) in CH$_2$Cl$_2$ (40 mL) was added a solution of ferrocenecarboxaldehyde (0.69 g, 3.22 mmol) and triethylamine in CH$_2$Cl$_2$ (20 mL). The mixture was refluxed for 24 h under nitrogen. After evaporation of the solvent, residue solid was washed with hexane twice to remove unreacted ferrocenecarboxaldehyde and dried in vacuum. Yield 80%; mp 113–115 °C; FTIR: 1640 cm^{-1} (CH=N); ^{1}H NMR (400 MHz, CDCl3): δ (ppm) 8.13 (s, 4H, C*H*N), 7.06 (d, 8H, *J*=7.2 Hz, Ar*H*), 6.71 (t, 4H, *J*=7.2 Hz, Ar*H*), 4.65 (s, C$_5$*H*$_4$, 8H), 4.35 (s, C$_5$*H*$_4$, 8H), 4.17 (s, C$_5$*H*$_5$, 20H), 3.69 (t, 8H, *J*=6.6 Hz, OC*H*$_2$), 3.66 (s, 8H, ArC*H*$_2$Ar), 3.52 (t, 8H, *J*=6.6 Hz, NC*H*$_2$), 1.98 (p, 8H, *J*=6.6 Hz, OCH$_2$C*H*$_2$CH$_2$N); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 161.0, 156.6, 133.9, 130.1, 121.9, 70.5, 69.8, 69.2, 68.6, 59.0, 36.7, 32.0; HRMS calculated for C$_{84}$H$_{84}$N$_4$O$_4$Fe$_4$: 1436.9702. Found: 1436.9727.

Supplementary data

^{1}H, ^{13}C, APT, and COSY NMR spectra of compounds, cyclic voltammetry (CV), and UV–vis spectral data. Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2011.10.117.

References and notes

1. Bohmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713–745.
2. Asfari, Z.; Bohmer, V.; Harrowfield, J.; Vicans, J. *Calixarenes 2001*; Kluwer: Dordrecht, The Netherlands, 2001.
3. Gokel, G. W. *Crown Ethers and Cryptands*; Royal Society of Chemistry: Cambridge, UK, 1991.
4. Wenz, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 803–822.
5. Yilmaz, M.; Memon, S.; Tabakci, M.; Bartsch, R. A. In *New Frontiers in Polymer Research*; Bregg, R. K., Ed.; Nova: New York, NY, 2006.
6. Gutsche, C. D.; Iqbal, M.; Stewart, D. *J. Org. Chem.* **1986**, *51*, 742–745.
7. Erdemir, S.; Tabakci, M.; Yilmaz, M. *Tetrahedron: Asymmetry* **2006**, *17*, 1258–1263.
8. Memon, S.; Akceylan, E.; Sap, B.; Tabakci, M.; Roundhill, D. M.; Yilmaz, M. *J. Polym. Environ.* **2003**, *11*, 67–74.
9. Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609–1646.
10. Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516.
11. Snowden, T. S.; Anslyn, V. *Curr. Opin. Chem. Biol.* **1999**, *3*, 740–746.
12. Zlatuskova, P.; Stibor, I.; Tkadlecova, M.; Lhotak, M. *Tetrahedron* **2004**, *60*, 11383–11390.
13. Lehn, J. M. *Supramolecular Chemistry—Concepts and Perspectives*; VCH: Weinheim, Germany, 1995.
14. Atwood, J. L.; Davies, J. E.; Macnicol, D. D.; Vogtle, F.; Lehn, J. M. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, 1996.
15. Beer, P. D.; Gale, R. A.; Chen, Z. G. *J. Chem. Soc., Dalton Trans.* **1999**, 1897–1910.
16. Gao, Y. H.; Zhang, L. L.; Liu, Z. P.; Guo, D. S. *Chin. J. Org. Chem.* **2007**, *8*, 937–942.
17. Han, J.; Yan, C. G. *Prog. Chem.* **2006**, *12*, 1668–1676.
18. Evans, A. J.; Matthews, S. E.; Cowley, A. R.; Beer, P. D. *Dalton Trans.* **2003**, 4644–4650.
19. Beer, P. D.; Hayes, E. J. *Coord. Chem. Rev.* **2003**, *240*, 167–189.
20. Tomapatanaget, B.; Tuntulani, T. *Tetrahedron Lett.* **2001**, *42*, 8105–8109.
21. Tomapatanaget, B.; Tuntulani, T. *Org. Lett.* **2003**, *5*, 1539–1542.
22. Guo, D. S.; Liu, Z. P.; Ma, J. P.; Huang, R. Q. *Tetrahedron Lett.* **2007**, *48*, 1221–1224.
23. Chrisstoffels, L. A. J.; Jong, F.; Reinhoudt, D. N.; Sivelli, S.; Gazzola, L.; Casnati, A.; Ungaro, R. *J. Am. Chem. Soc.* **1999**, *121*, 10142–10151.
24. Molins, M. A.; Nieto, P. M.; Sanchez, C.; Prados, P.; de Mendoza, J.; Pons, M. O. *J. Org. Chem.* **1992**, *57*, 6924–6931.